

Phase Structure of Symmetric Tri-Block-Copolymers and their Blends

Abstract

The series of block-copolymers PEO-*b*-PPO-*b*-PEO were selected for study. Block copolymers differ in the lengths of their blocks and in the weight fractions of their components. As the second component of blends, we used two narrow molecular weight fractions of neat polymer PEO. One PEO fraction ($M_w \sim 2000$) can crystallise as 'extended chains' (EC) only; the second ($M_w \sim 3000$) is more flexible, and is able to fold. The structure development was studied during slow heating of a well-crystallised system and during subsequent very slow cooling from the melt. The samples form different structures (lamellar, hexagonal and cubic) which change during both treatments. Pure PEO components crystallise in all blends as EC. The periodicities formed in the structures are proportional to the molecular weight of pure PEO. The growth of periodicities (lamellar thickening) occurs as heating approaches the melting point. The components of copolymers are not compatible; they are phase-separated in the melt also, which is demonstrated by the periodical structure observed by SAXS. The melt-periodicities are proportional to the molecular weight of copolymers. The growing structural periodicities in melted blends, together with the increase in the content of pure polymer, indicate the dilution of phase-separated PPO regions in the melt.

Key words: crystallisation, block copolymers, blends, SAXS, WAXS.

Introduction

Block copolymers are of great scientific interest due to their self-assembled supramolecular structures formed under various conditions [1, 2]. In crystalline/amorphous copolymer systems, three factors determine the final phase and crystalline morphology, i.e. the microphase separation of block copolymer, the crystallisation of crystallisable blocks, and the vitrification of the amorphous blocks. The phase separation behaviour of block copolymers results in the creation of lamellar (L), hexagonal (H) and cubic (C) structures depending on the different environments of the assembling copolymer molecules. Each of these structures is generally nanoscale in size, and varies its morphology and function with changes in chemical structure and composition.

Extensive studies have been devoted in the last decade to the important family of polymer/copolymer blends, where the homopolymer is identical with one block of the copolymer used [3, 4]. The major part of these studies was devoted to blends, where both the constituents of blends were amorphous. However, very little is known about the blends where the block copolymer consists of an amorphous and crystalline component, and the crystalline component is the same as homopolymeric admixture. In this case the co-crystallisation in blends can be observed. The extent of co-crystallisation

strongly depends on melting points, crystallisation rates, molecular weights and the molecular weight distribution of components [5-9]. The architecture and structural diversity of block copolymers are reflected in their complicated structure formation, as well as in the different kinetics of structure developments and transformations in their blends with pure polymer. In the case of crystallisable components in the systems, the structure formation is dependent not only on phase separation phenomena but also on the ability of components to crystallise or co-crystallise.

The aim of this work was to study the structural phenomena occurring in the series of two-component symmetrical tri-block-copolymers and their blends with neat polymer during heat treatments to obtain a thorough insight into the structure formation and the kinetics of transformation of blend morphologies depending on process variables. A series of PEO-*b*-PPO-*b*-PEO block-copolymers were selected for the study. Block copolymers differ in the lengths of their blocks and in the weight fractions of their components. Two narrow molecular weight fractions of neat polymer PEO were used as the second component of the blends. One fraction of PEO ($M_w \sim 2000$) is a 'stiff' unit, as it can crystallise as EC only; the second is flexible, as it is able to crystallise in EC or in a once fold chain (1F) form during crystallisation [10-14]. The

structure development was studied by WAXS, SAXS and DSC during very slow cooling from the melt and during slow heating of a well-crystallised system. Special attention was paid to the development of different types of nanostructures, and to the roles of copolymer compositions and of amorphous blocks (PPO) in the process of morphology development and transformations.

Experimental

Materials

The poly(ethylene oxide) used consisted of two hydroxyl-terminated low molecular-weight fractions of $M_w \sim 2000$ and 3000 (P2, P3) supplied by Fluka AG, and four different Pluronic samples; symmetrical tri-*block* copolymers PEO-*b*-PPO-*b*-PEO- $E_i P_j E_i$ (i, j are the numbers of ethylene oxide E and propylene oxide P monomer units) supplied by BASF, SIGMA and SERVA were used. The structural characteristics of all the samples are summarised in Table I. The block copolymers differ in molecular weights and in the lengths of E and P blocks. The lengths of E blocks are comparable to the lengths of the second components of the blends (P2, P3). The neat PEO samples are highly crystalline ($\sim 80\%$). The crystallinities of block copolymers are much lower ($\sim 40\%$), as the P blocks are amorphous and the E chains' mobility is reduced through their binding to PPO.

Table 1. Parameters of studied polymers.

Samples	P, M _w	E, M _w	E, %	I _E , Å	I _P , Å	Cr, %	LP _M , Å
P 105 E ₃₇ P ₅₆ E ₃₇	3250	2x1625	50	103	196	29	84
P 6800 E ₈₀ P ₃₀ E ₈₀	1750	2x3500	80	221	105	45	–
F 127 E ₁₀₀ P ₆₅ E ₁₀₀	3780	2x4410	70	278	228	41	116
F 108 E ₁₃₃ P ₅₀ E ₁₃₃	2920	2x5840	80	369	176	47	134
POE 2000 E ₄₅	–	2000	100	125	–	78	–
POE 3000 E ₆₈	–	3000	100	190	–	78	–

P_n - PPO, E_n - PEO, n – number of monomer units; I_P, I_E - lengths of chains; Cr – crystallinity; LP_M – periodicity in melt

Table 2. Melting T_m and crystallization T_c temperatures of BCPs and their blends with polymers P2 and P3.

Sample	BCP	P2		P3	
	w _{BCP}	T _c , °C	T _m , °C	T _c , °C	T _m , °C
P 105	1.0	31.0/32.0	46.5/48.9		
	0.8	32.6/34.8	55.9	36.1/38.4	54.8
	0.6	37.5	57.0	42.3	61.8
P 68	1.0	37.4	56.4		
	0.8	38.5	57.9	39.8	59.4
	0.6	38.7	58.4	43.2	61.6
F 127	1.0	37.0	53.4		
	0.8	41.4	61.2	44.1	62.3
	0.6	40.9	60.8	44.1	63.4
F 108	1.0	45.6	61.7		
	0.8	43.9	61.3	46.0	62.4
	0.6	42.8	61.0	45.0	62.4

Table 3. Structure changes of copolymer P105 and its blends with polymers P2 and P3 during heating and cooling.

Blend	w _{P105}	Cooling			
		LP, Å	Nanostructure	LP, Å	Nanostructure
P 105 / P2	1.0	226-300	C29/M47	287	L
	0.8	288-342	L29/C46/M53	306-307	M50/C48
	0.6	196-446	L29/C48/M53	294-282	M49/C48
	0.4	174-183	L28/M56	300-270	M53/C52*
	0.2	152-201	L26/M54	249-277	M51/C50
P 105 / P3	0.8	207-277	L25/C46/M60	260-277	M50/C49
	0.6	219-241	NI	294-277	NI
	0.4	219-249	L25/C50/M57	288	M53/C50/L34
	0.2	226-249	C25/L52/M60	219-288	M51/L50/C42

LP - periodicities, L29 - structure type and temperature of transformation, * probable type of structure, NI - not identified structure.

Block copolymers and their blends (8/2, 6/4, 4/6 and 2/8 by weight) with PEO were prepared by dissolving in chloroform and subsequent drying at 40°C for 5 days in vacuum. Such prepared-annealed samples were used for WAXS and for time-resolved SAXS experiments.

WAXS and SAXS

The WAXS diffraction patterns were obtained using an HZG/4A powder diffractometer (Seifert GmbH, Germany). The crystallinities were estimated by us-

ing integral intensities diffracted by the crystalline and amorphous phases.

Time-resolved SAXS measurements were performed on a reconstructed Kratky camera and on an Austrian SAXS beamline at the Elettra synchrotron in Trieste. A 1.6 mm-thick sample in a special holder was inserted into the heating chamber placed in the X-rays' path. The samples were measured at room temperature, then measured during heating in 1°C steps from 35°C to melt, and subsequent cooling

from the melt to 35°C. The samples were maintained at each temperature for 20 min. (10 min. annealing and 10 min. SAXS measurement). The slow heating and cooling rate was chosen with the aim of measuring scattering curves of the structure characteristic of the measured temperature. The scattering curves measured with the Kratky camera were de-smearred, and all the curves were Lorentz-corrected. Peak positions were employed to obtain periodicities according to Bragg's law, $LP=2\pi/q$ ($q=4\pi/\lambda$)sin θ, where λ is the wavelength and 2θ is the scattering angle.

The DSC was carried out on a Perkin Elmer DSC-2 calorimeter and DSC/SAXS equipment at the Elettra SAXS beamline. The values of melting T_m and crystallisation T_c temperatures are shown in Table II.

Results and discussion

Blends P105/P2,P3

– E₃₇P₅₆E₃₇/E₄₅E₆₈

Block copolymer P105 has the shortest E₃₇ tails (105 Å); the lowest T_m and high weight fraction of P₅₆ block causes the lowest crystallinity in the BCPs series. One dominant SAXS maximum at the lowest angles (226 Å) with only a shoulder at higher angles is not enough to determine the type of structure. This periodicity steeply increases approaching T_m. During cooling from the melt, a lamellar structure with a periodicity of 287 Å is formed.

In Figure 1, the development of the scattering curves of the P105/P2 8/2 blend during heating and cooling is displayed. In this figure, only the selected characteristic SAXS curves obtained during this procedure are shown. The initial lamellar (L) structure changes at 46°C to a cubic (C) structure, and this structure melts at 53°C. The molten blend starts to crystallise at 49°C in the C structure, and the structure of type C does not change during cooling. The quality of this structure improves during cooling, but does not reach the level of the order of annealed blends. A similar development of structures was observed for the whole composition series of P105/P2 blends. In blends 4/6 and 2/8, only an L structure exists during cooling. C and L structures are observed during crystallisation from the melt. The P105 blends with P3 have similar behaviour. Also here, the blends

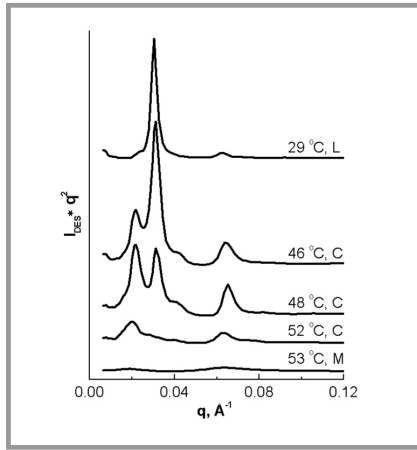


Figure 1. Development of SAXS curves of P105/P2 (8/2) blend during heating.

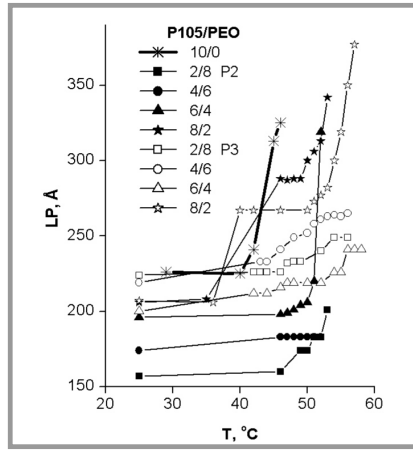


Figure 2. Changes in SAXS LP periodicities of blends P105 with P2 and P3 during heating.

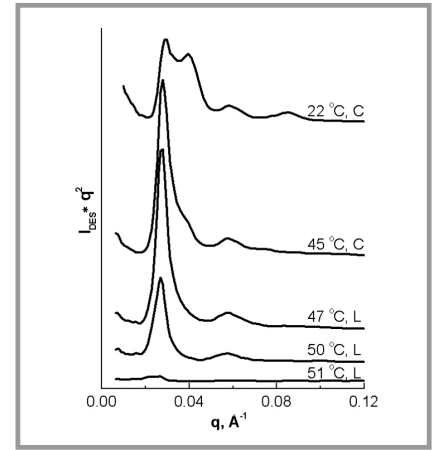


Figure 3. Development of SAXS curves of copolymer P68 during heating.

crystallise in L and C structures with better developed order in the annealed samples than after the crystallisation from the melt.

In Table 3, maximum periodicities (LP, the types of nanostructures in P105 and in blends and the temperatures of structure transformations are summarised. From Table 2 it follows that the LPs are much more sensitive to heating than to cooling. While the LPs practically do not change during cooling, they increase when the heating approaches melting point (Figure 2). This growth could be ascribed to the improvement of the crystalline part of the lamellae. Steep LP growth near T_m exists in neat BCP, similarly to what happens in blends with a minimal content of PEO admixtures. The structural development in these blends is controlled by the dominant component, that is, neat BCP. The growth in LPs could be explained by the structure transformation, and/or by the thickening of amorphous interlayers caused by partial melting of the shortest E chains in blends and their diffusion in these regions. The slow crystallisation of blends during cooling from melt causes the formation of a very stable high temperature structure, in which LPs do not change during the treatment.

LPs in blends with P2 are smaller than in blends with P3. In both cases they are larger than are the lengths of P2 and P3 chains respectively. The crystalline part of the lamellae consist (at least in L structures) of EC P2, P3 and E blocks of BCP. The LPs in annealed blends with P2 increase with the decrease in the contents of neat polymer. The growing content of BCP in blends means an increase in the content of amorphous P blocks, and con-

sequently a thickening of the amorphous interlayers. In blends with P3 these changes are small. The driving force for structural development in blends is crystallisation and phase separation. Neat polymers have a strong tendency to co-crystallise with the E tails of BCP. The length of E blocks of copolymer~103 Å is comparable with the length of P2~125 Å, but it is practically one-half of the length of P3~190 Å. A small thickening of crystalline parts of lamellae in blends with P2 is caused by the growing content of longer P2 chains. In the case of blends with P3, crystalline parts of lamellae co-crystallised in the EC form of the P3 are parallel with pairs of the extended E tails of BCP, and in such kind of lamellae there is small space for thickening.

Blends P68/P2,P3



BCP P68 is composed of a middle block P_{30} of 105 Å long and two E_{80} blocks of 221 Å long. Owing to the P content, it has a crystallinity of about 0.45. The develop-

ment of the SAXS curves of neat P68 during heat treatment is shown in Figure 3. The structure of annealed sample is C, and during heating it changes at 47°C to an L structure, which melts at 53°C. The melt starts to crystallise at 43°C in the C structure, and this structure is preserved up to room temperature. LP starts at 216 Å, and near T_m it increases to 257 Å.

The SAXS scattering curves of annealed P68/P2 8/2 and 6/4 blends indicate the C structures, which transform after heating to 50°C to L structures and melt at temperatures of 55°C for blend 8/2 and 53°C for blend 6/2. These molten blends start to crystallise at 45°C in L structures, and this structure does not change during further cooling. Annealed blends with compositions of 4/6 and 2/8 have L structures which melt at 48°C and 53°C respectively. During cooling from the melt, both blends crystallise to an L structure, which in 2/8 blend transforms at 45°C to a C structure. The development of structures of P68 blends with P3 is slightly different. The

Table 4. Structure changes of copolymer P68 and its blends with polymers P2 and P3 during heating and cooling.

Blend	Heating			Cooling	
	w_{P68}	LP, Å	Nanostructure	LP, Å	Nanostructure
P 68 / P2	1.0	216-257	C22/L47/M53	253-233	M44/C43
	0.8	221-241	C26/L50/M55	219-211	M46/L45
	0.6	185-312	H29/C50/M53	222-201	M46/L45
	0.4	166-193	L29/M59	183-174	M48/L47
	0.2	159-201	L29/M58	201-183	M53/L52/C45
P 68 / P3	0.8	219-327	C28/L58/M63	249-219	M52/C50
	0.6	226-272	L29/M63	293-277	M48/L46*
	0.4	222-241	L29/M62	272-241	M52/L51
	0.2	219-260	L29/M62	253-225	M52/L51

LP - periodicities, C22 - structure type and temperature of transformation, * probable type of structure.

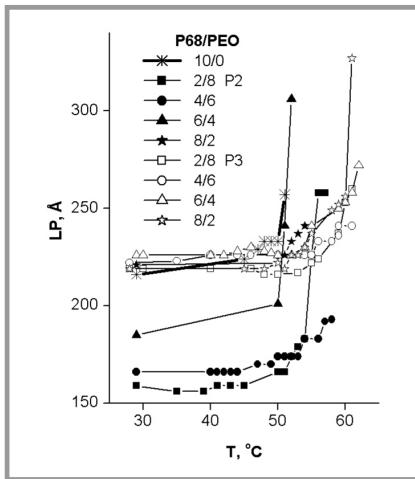


Figure 4. Changes in SAXS LP periodicities of blends P68 with P2 and P3 during heating.

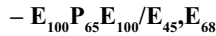
annealed blend 8/2 has a C structure, which changes to an L structure near the T_m of blend. During cooling from the melt, this blend crystallises into a C structure without further transformation. Blend 6/4 starts with an L structure and does not change up to melting. Cooling from the melt caused the crystallisation of the blend in a C structure. In blends 4/6 and 2/8 the only L structure exists during heating and also during cooling. P68 blends with P2 and P3 are better developed in annealed samples than after crystallisation from the melt.

In Table 4, the LP periodicities, the types of nanostructures and the temperatures of structure transformations in P68 and blends are summarised. Table 4 shows that the LPs are more sensitive to heating than to cooling. While LPs practically do not change during cooling, they increase as they are heated towards melting point (Figure 4). The small growth could be explained by the improvement of the crystalline part of lamellae. Steep LP growth near T_m exist in neat BCP and in some blends (P68/P2 6/4, 2/8 and P68/P3 8/2). The LP growth could be explained by the thickening of amorphous interlayers caused by the partial melting of the shortest E chains and their diffusion in these regions.

LPs in P68 blends with P2 are smaller than in blends with P3 (Figure 4). In both kinds of blends their values are greater than are the lengths of P2 and P3 chains respectively. Neat polymers have a strong tendency to co-crystallise with the E tails of BCP. The E blocks of copolymer (~221 Å) are twice as long as the P2 chains and slightly longer than the P3

chains. The crystalline part of lamellae consists of EC of P2 or P3 and 1F of E blocks of BCP for blend with P2 and EC in blend with P3. The LPs in annealed blends of P68 with P2 increase with the increase in the contents of neat polymer. In blends with P3, LPs are practically the same for all compositions. The slow crystallisation of blends during cooling from melt causes the formation of a very stable high-temperature structure, in which LPs do not change during this treatment.

Blends F127/P2,P3



BCP F127 is composed of a middle block P_{65} of 228 Å long and two E_{68} blocks of 278 Å long. It has a crystallinity of about 0.45. The structure of the annealed sample is L. The SAXS scattering curves measured during heating are not well developed. The structure could probably be C at 52°C. This structure melts at 56°C. The melt starts to crystallise at 46°C in the H structure, and transforms to an L structure at 43°C. The LPs increase during heating from 203 Å to 331 Å; during cooling the LP is 197 Å.

Table 5. Structure changes of copolymer F127 and its blends with polymers P2 and P3 during heating and cooling.

Blend	w_{F127}	Heating		Cooling	
		LP, Å	Nanostructure	LP, Å	Nanostructure
F 127 / P2	1.0	203-331	L27/C52/M56	197	M47/H46/L43
	0.8	183-334	L26/C58/M59	206	M54/H52/L47
	0.6	183-387	L26/M57	210	M51/H50/L48
	0.4	206-219	L25/M58	215	M52/H50/L49
	0.2	183-212	L24/M58	166	M48/C47*
F 127 / P3	0.8	183-267	H24/L55/M60	206	M51/H50
	0.6	267-296	C24/L56/M61	232	M52/H51/L48
	0.4	215-300	L25/M62	258	M52/H61/L48
	0.2	219-288	L24/M60	249	M49/L48

LP - periodicities, L27 - structure type and temperature of transformation, * probable type of structure.

Table 6. Structure changes of copolymer F108 and its blends with polymers P2 and P3 during heating and cooling.

Blend	w_{F108}	Heating		Cooling	
		LP, Å	Nanostructure	LP, Å	Nanostructure
F 108 / P2	1.0	377-446	L25/C55/M59	219	M49/L48
	0.8	319-421	L25/H52/M57	225-212	M50/L49
	0.6	212-313	L25/M60	219	M53/L52
	0.4	175-241	L25/M59	200	M51/L50
	0.2	159-257	L25/M58	241-222	M53/L52/C49
F 108 / P3	0.8	273-306	C26/L59M63	264-259	M54/C52
	0.6	249-289	L25/M63	249-226	M53/L52
	0.4	226-277	L25/M61	267-258	M52/L51
	0.2	219-288	L25/M61	256-258	M50/L48

LP - periodicities, L25 - structure type and temperature of transformation,

Blends of annealed F127 with P2 and P3 display a complicated structure development. Three different structure modifications, L, C and H, occur here during heating and cooling. The annealed blends with P2 have an L structure which does not change for compositions 6/4, 4/6 and 2/8 up to melting around 57°C. In blend 8/2, the starting L structure transforms at 58°C to a C structure and melts at 59°C (Figure 5). The molten blends 8/2, 6/4, 4/6 start to crystallise around 50°C in H structures, and this structure transforms to L after about 2°C of cooling. For the 2/8 blend, which crystallises at 47°C, it was not possible to determine the type of structure from the SAXS curves.

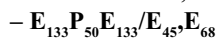
The development of the structures of blends F127 with P3 is slightly different. The annealed blend 8/2 has an H structure, which changes to an L structure at 55°C and melts at 60°C. During cooling from the melt, this blend crystallises as H. The initial C structure in blend 6/4 transforms to L at 56°C and melts at 61°C. The cooling from the melt caused the

crystallisation of the blend in an H structure which recrystallises to an L structure. In blend 4/6 and 2/8, the only L structure exists during heating. During the cooling of 6/4 blend from melt, it crystallises in an H structure, which changes to an L structure, while blend 2/8 crystallises in L without further change. Blends F127 with P2 and P3 are better developed in annealed samples than after crystallisation from the melt.

In Table 5, the LP periodicities, the types of nanostructures and the temperatures of structure transformations are summarised. The LP periodicities (Figure 6) in neat BCP and in blends with P2 8/2, 6/4 steeply increase as heating approaches T_m . The LP growth could be explained by the thickening of amorphous interlayers caused by partial melting of the shortest E chains in blends and their diffusion in these regions. The LPs in the rest of the blends increase more slowly during heating. This effect is more pronounced in blends with P3. The growth is caused by the improvement of the crystalline part of the lamellae.

The LPs in BCP blends with P2 are smaller than in blends with P3 (Figure 6). In both kinds of blends, their values are greater than the lengths of the P2 and P3 chains respectively. Neat polymers have a strong tendency to co-crystallise with the E tails of BCP, which are much longer (~278 Å) than P2 and P3 chains. The crystalline parts of the lamellae consist of EC P2 or P3, and of 1F of E blocks of BCP. The LPs in blends of F127 with P2 are smaller than in blends with P3, owing to the chain lengths of these components. The slow crystallisation of blends during cooling from melt causes the formation of very stable high-temperature structures in which LPs do not change during this treatment.

Blends F108/P2,P3



The copolymer F108 is composed of a middle block P_{50} of 176 Å long and two E_{133} tails of 369 Å long. The tails are the longest in the BCP series. The crystallinity is about 0.47. The SAXS scattering curves measured during heating are shown on Figure 7. The structure of annealed sample is L. At 55°C it transforms to a C structure, which is connected with an abrupt increase in LPs. This structure melts at 59°C. The melt starts to crystallise at 48°C in an L structure without further changes.

The annealed blend of F108 with P2 has an L structure, which recrystallises during heating at 52°C, probably to an H structure, and melts at 57°C. This blend crystallises during cooling from the melt at 42°C in an L structure. The annealed blends 6/4, 4/6 and 2/8 have an L structure, in which LPs periodicities increase during heating. These lamellar structures melt at around 52°C. All molten blends start to crystallise around 50°C in L structures, and this structure does not change during cooling. Only blend 2/8 recrystallises at 42°C to a C structure. A similar structural development was observed in blends F108 with P3. Annealed blends, with the exception of blend 8/2, have an L structure during both cooling and heating. The LPs of annealed blends increase during heating, while during cooling from the melt the periodicity remains constant. The annealed blend 8/2 has a C structure which recrystallises at 59°C to an L structure and melts at 63°C. During cooling, this blend starts to crystallise at 52°C

without further changes. Blends P127 with P2 and P3 are better developed in annealed samples than after crystallisation from the melt. The recrystallisation behaviour of annealed structures in F108 and in blends F108/P2 and F108/P3 of 8/2 composition are similar, and are controlled by the dominant F108 constituent.

In Table 6, LP periodicities, the types of nanostructures during heating and the temperatures of structure transformations are summarised. The LPs (Figure 8) increase similarly with the increase in temperature in neat BCP F108 and in all blends. The steepest growth of periodicity LP is in neat F108. The slower growth of LP reveal blends with P2, and moderate growth of LPs exists in blends with P3. The steep LPs growth could be explained by the recrystallisation and/or by the thickening of amorphous interlayers caused by partial melting of the shortest E chains and their diffusion in these regions.

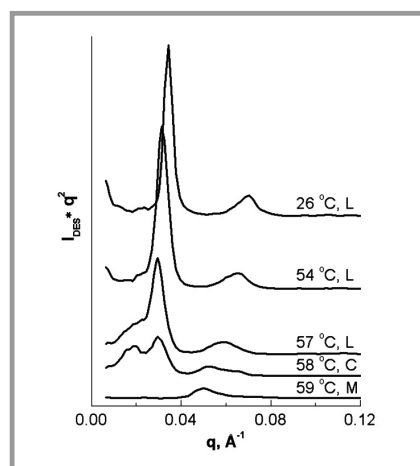


Figure 5. Development of SAXS curves of 127/P2 (8/2) blend during heating.

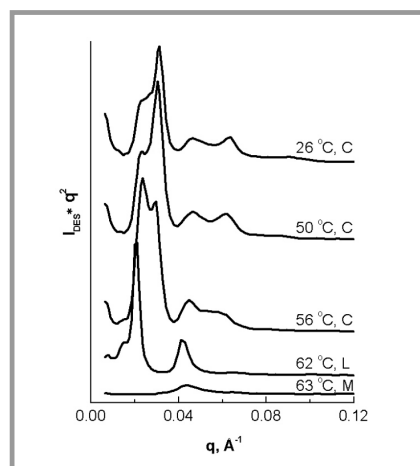


Figure 7. Development of SAXS curves of F108/P3 (8/2) blend during heating.

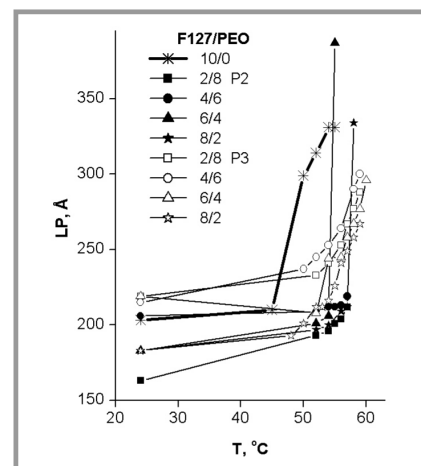


Figure 6. Changes in SAXS LP periodicities of blends F127 with P2 and P3 during heating.

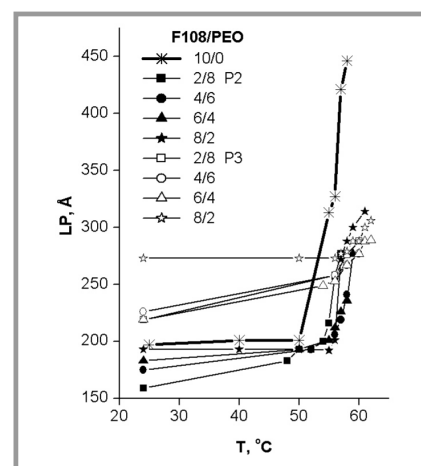


Figure 8. Changes in SAXS LP periodicities of blends F108 with P2 and P3 during heating.

LPs in F108 blends with P2 are smaller than in blends with P3 (Figure 8) as the P2 chains are shorter than P3 chains. The periodicities LPs in both kinds of blends are greater than are the lengths of P2 and P3 chains respectively. Neat polymers have a strong tendency to co-crystallise with the E tails of BCP, which are much longer (~369 Å) than the P2 and P3 chains. The crystalline parts of the lamellae consist of EC P2 or P3 and of twice-folded E blocks of BCP with P2 and 1F of E block with P3. The slow crystallisation of blends during cooling from melt causes the formation of very stable high-temperature structures in which LPs do not change during further temperature treatment.

BCPs and blends in melt

The melt block copolymers and their blends with homopolymers can self-assemble into a variety of ordered structures via the process of microphase separation. The E and P components of studied systems are not miscible in the melt. For this reason, they consist in melt systems of two separated phases, namely clusters of P chains in an E-chain matrix. The SAXS

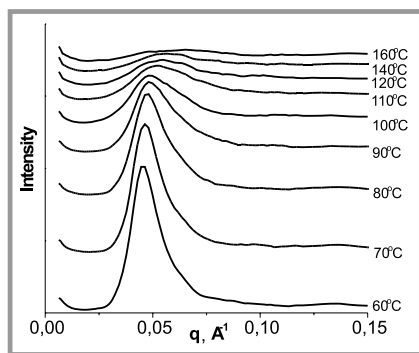


Figure 9. Changes of SAXS curves of melted co-polymer F108 during heating.

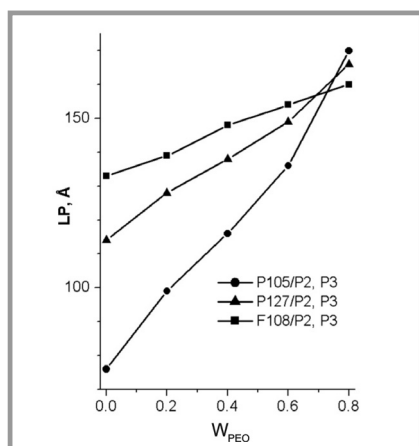


Figure 10. Increase of LP periodicities in melted blends with increase in content of neat PEO.

curves of neat BCP reveal only a first-order maximum. The LPs obtained from these curves increase with the increase in molecular weight of the BCPs (Table 1). The scattering curve of P68 has no maximum. Very short P blocks are very 'diluted' with the second component in this case, and probably form very small and disturbed clusters with insufficient electron density difference from the E matrix to reveal an SAXS maximum.

The existence of the order-disorder transition temperature in neat BCP samples can be studied using temperature-dependent SAXS. The SAXS curves of our samples were measured within the range of 70°C to 180°C (Figure 9). With the increase in temperature, the scattering peak shows a slight shift of the peak position towards higher q values. The scattering intensity of this peak gradually decreases, which is accompanied by a broadening of the reflection. This behaviour of SAXS curves corresponds to the ordered melt structure. No abrupt change in the intensity of the SAXS reflection, which would indicate order-disorder transition [15], was observed.

The ordered structures also appear in the melts of BCPs blends with P2 and P3. The LPs increase with the increase in concentration of homopolymers in the blends, as shown on Figure 10. The values of LPs and their changes with the increase in content of P2 and P3 are practically the same. The increasing content of homopolymers 'dilutes' the P clusters in the E matrix.

Conclusions

The neat copolymers and their blends with P2 and P3 form different structures (L, H, and C) which change during both treatments. Neat homopolymers co-crystallise with the tails of BCP in EC form in all blends. The E tails of P105 co-crystallise in blends with P2 and P3 in EC form, in P68 blend with P2 in 1F and with P3 in EC forms, in F127 blend with P2 and P3 in 1F forms and in F108 with P2 in 2F and with P3 1F forms.

The LP periodicities formed in all blends are proportional to the molecular weights of neat PEO components. The steep growth of LPs, which proceeds in the systems studied as heating approaches the melting point, can be explained by the structural transformation of the crystalline phase and/or by the thickening of amorphous interlayers caused by partial

melting of the shortest E chains in blends and their diffusion into amorphous regions. The slow crystallisation of blends during cooling from melt causes the formation of a very stable high-temperature structure; the LPs changes are therefore small during the proceeding decrease in temperature.

The components of copolymers are not compatible; they are phase-separated in the melt also, as is demonstrated by the periodical structure observed by SAXS. The melt-periodicities are proportional to the molecular weight of copolymers. Growing structural periodicities in melted blends with the increase in the content of pure polymer indicate the 'dilution' of phase-separated PPO regions in the melt. □

Acknowledgments

Research was supported by the Grant Agency of the Czech Republic (grant No. 203/03/0611) of the Academy of Sciences of the Czech Republic, project No.: AVOZ 40500505.

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□ Received 08.12.2004 Reviewed 10.02.2005