Phase behaviour in poly(ethylene oxide-*b*-t-butyl methacrylate) block copolymers

R. Unger, D. Beyer and E. Donth*
Department of Physics, Technical University Merseburg, D-0-4200 Merseburg, Germany
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The lamellar thickness of the poly(ethylene oxide)-poly(t-butyl methacrylate) (PEO-PTBMA) diblock copolymer system, obtained by differential scanning calorimetry and small angle X-ray scattering investigations, is correlated with the degree of polymerization of the amorphous (PTBMA) and crystallizable (PEO) sequences. The non-equilibrium exponents obtained immediately after bulk crystallization are different to those from extrapolated equilibrium results. Within the experimental standard deviations, the theoretical predictions of DiMarzio *et al.* and of Whitmore and Noolandi could be confirmed. The molecular weights of PEO and PTBMA ranged from 250 to 21 000 g mol^{-1} and from 1500 to 17 000 g mol^{-1}, respectively. Both the equilibrium lamellar thickness l and the PEO domain size d_{PEO} increase with increasing PEO and decreasing PTBMA degrees of polymerization Z according to $d_{PEO} \sim l \sim Z_{EO}^{0.97 \pm 0.08} Z_{TBMA}^{-(0.53 \pm 0.19)}$.

INTRODUCTION

This paper is concerned with the phase behaviour in thermodynamic non-equilibrium and equilibrium of diblock copolymers with one crystallizable component.

Besides the synthesis of new monomers and polymers, and the mixing of polymers, block copolymerization represents an additional method of production of new materials. Although this is technologically expensive, copolymerization makes the combination of polymers and monomers with opposite properties possible, even in the case of incompatible polymers (for instance, hydrophilic-hydrophobic, crystalline-amorphous, adhesive-cohesive, polar-non-polar, elastic-plastic and others). It leads, nevertheless, to homogeneous materials in the micrometre range.

Many theoretical and experimental papers have dealt with the question of what kinds of domain can be formed in equilibrium and of which size they are. As a rule, only block copolymers with two amorphous components are dealt with.

The aim of theoretical work is the description of the thermodynamic equilibrium structure of copolymers. In the paper of Meier[1], the most important elements were pointed out for the first time. Using the theories of equilibrium thermodynamics (random-walk statistics) and the mean-field approximation, Helfand and Wasserman[2], Kawasaki *et al.*[3], Leibler[4], Hong and Noolandi[5,6] and Ohta *et al.*[7] made considerable progress in the theory of domain formation.

Essentially, the domain size and form are defined by the free energy of interface formation (it tends to the largest possible phase growth), the free energy contribution based on restrictions due to the necessary positioning of the block joint in the phase interface, and the free energy contribution connected with the requirement of constant polymer density in the domains. Polymer compatibility and, connected with this, the interface properties also play an important role.

In the case of strong segregation (or narrow interface approximation) the domain size in equilibrium is given by:

$$d = c(f, \Phi, \chi_{12}, b_K) Z^{2/3} T^{-1/3} \qquad (1)$$

where the constant c depends on monomer fraction f, volume fraction Φ, Flory-Huggins interaction parameter χ_{12} and Kuhn statistical segment length b_K; Z is the degree of polymerization of the block copolymer segment considered, and T is the temperature. The deviation from the Gaussian dimensions of a polymer coil ($r \sim Z^{1/2}$) is the result of chain stretching in the domains as a consequence of the homogeneous density requirement.

Kämpf *et al.*[8-10] experimentally found spherical, cylindrical and lamellar domain structures for increasing weight fractions. The theoretical estimation of the monomer fractions at which phase transitions occur is very difficult, because the difference in free energy of these three structures is only small.

The relationship $d \sim Z^{2/3} T^{-1/3}$ was confirmed, e.g. by Hashimoto *et al.*[11-13] using lamellar and spherical domains of polystyrene-polyisoprene block copolymers.

The investigation of block copolymers with a crystallizable component (abbreviated as crystalline-amorphous block copolymers) demands consideration of driving forces due to the crystallization. In the homopolymer a non-equilibrium lamellar crystal is formed by chain folding. Under certain conditions, an extended-chain crystal is formed by annealing (this is then equilibrium). In contrast, in crystalline-amorphous block copolymers, a folded crystal is formed in equilibrium[14]. This state is, similarly to amorphous-amorphous block copolymers, a consequence of the tendency to constant density in the domains.

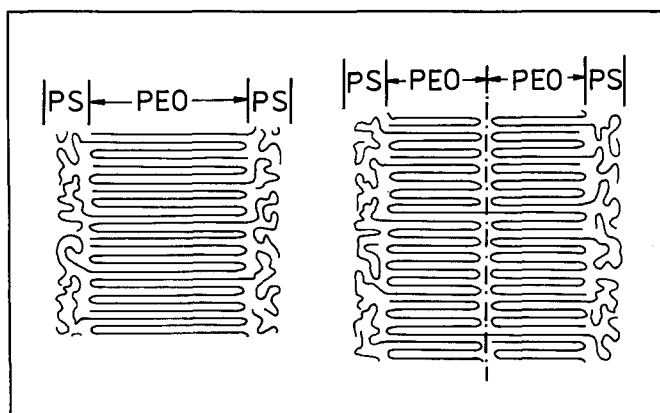* To whom correspondence should be addressed

Figure 1   PEO-PS crystallization models for single-layer and double-layer structures (from ref. 15)

For an incompressible system and using Gaussian chain statistics, the equilibrium dimensions of a lamellar domain arrangement of semicrystalline and amorphous layers were calculated by DiMarzio *et al.*[14] for diblock copolymers:

$$d_{cr} \sim Z_{cr}^{1} Z_{am}^{-1/3} T^{-1/3} \tag{2a}$$

$$d_{am} \sim Z_{am}^{2/3} T^{-1/3} \tag{2b}$$

respectively, where Z_{cr} and Z_{am} are the degrees of polymerization of crystalline and amorphous blocks, respectively.

The investigations of Lotz and Kovacs[15] and of Gervais and Gallot[16,17] on poly(ethylene oxide)-polystyrene (PEO-PS) and poly(ethylene oxide)-polybutadiene (PEO-PB) block copolymers led to the structure models shown in *Figure 1*. (The structure is to be continued on both sides.) The single-layer (PEO) model represents the smaller free energy. Only lamellar microphase structures were observed[16,17] in experiments, at least for relatively large fractions of the crystallizable component ($\geqslant 10$ wt%).

Using the modern mean-field approximation described by Hong and Noolandi[5,6], Whitmore and Noolandi[18,19] also calculated the equilibrium structure of crystalline-amorphous diblock copolymers. The free energy contribution due to crystallization was taken into consideration in addition to contributions like those for amorphous-amorphous block copolymers. The following formulae were obtained for equilibrium:

$$d_{cr} \sim Z_{cr}^{1} Z_{am}^{-5/12} E_{f}^{1/3} T^{-1/3} \tag{3a}$$

$$d_{am} \sim Z_{am}^{7/12} E_{f}^{1/3} T^{-1/3} \tag{3b}$$

where E_{f} is the energy for chain folding. The formulae almost correspond to the results of DiMarzio *et al.*[14] (see equation (2)). The number of folds per chain is given by:

$$n_{f,eq} \sim Z_{am}^{5/12} T_{f}^{1/3} E^{-1/3} \tag{4}$$

which means that the number of folds is *independent* of the degree of polymerization of the crystalline block. The following conclusions were made:

(i) The free energy and the chain stretching of the amorphous layer can be described in a similar manner as for amorphous-amorphous copolymers.
(ii) The free energy of the crystalline layer is mostly defined by the energy of chain folding.

By means of SAXS and d.s.c., Gervais and Gallot[16,17] have investigated the crystallization and phase behaviour of several diblock copolymers and star-shaped copolymers (two PEO blocks linked at the same end of an amorphous block): PS-PEO, PB-PEO, PS-poly(ε-caprolactone) and poly(4-t-butylstyrene)-PEO. The main aim was to investigate the phase behaviour in the presence of a (preferential) solvent below and above the PEO melting point. Below 50°C (323 K), a lamellar domain arrangement was found in all cases in both the dissolved and the unsolved state. PEO crystallized in double-layer folded crystals. The greater the solvent fraction, the thicker the lamellae and the smaller the number of chain folds. There is an influence of block length and chemical structure (linear or branched copolymers) on the layer thickness that favours[19] some points of the theoretical approaches mentioned.

PEO-poly(t-butyl methacrylate) (PTBMA) diblock copolymers are investigated in this paper. PTBMA is the amorphous component. The system PEO-PTBMA is incompatible in both the melt and the supercooled melt[20,21].

The main aim of this paper is to make quantitative statements on the extrapolated equilibrium and non-equilibrium dimensions of crystalline lamellae in these block copolymers.

EXPERIMENTAL

Materials

The diblock copolymers were synthesized[22] by sequential anionic polymerization of ethylene oxide (EO) and t-butyl methacrylate (TBMA) using cumyl potassium (α,α-dimethylbenzyl potassium) as initiator. EO was distilled into the initiator solution at 195 K. The solution was kept at 313 K for between 54 and 186 h. Then a fixed amount of TBMA was slowly added (298 K). The polymerization of TBMA was terminated with 2-propanol after 30 min. The solvent was removed and all resulting polymers were stored over P_2O_5. The samples were extracted with water and were found to be free of homo-PEO.

The PTBMA part of the diblock copolymers was checked by i.r. spectroscopy in $CHCl_3$ using a Carl Zeiss (Jena) M80 instrument ($v(C=O)$ at 1717 cm^{-1}). The tacticity of PTBMA was determined by ^{13}C n.m.r. (22.635 MHz) in $CDCl_3$ ((65 ± 5)% syndiotactic). The glass transition temperature was found to be within the interval between 330 and 390 K corresponding to molecular weights of 3000 to 50 000 g mol^{-1} (strong dependence on molecular weight and tacticity).

All samples are documented in *Table 1*. Unfortunately, the absolute values of molecular weights are more uncertain than suggested by the random errors of the table. Thus, all information (for instance, the number of folds) has some additional uncertainties in this respect.

Methods

Calorimetric investigations were carried out by means of a DSC 2C apparatus (Perkin Elmer) using heating and cooling rates of $|dT/dt| = 10$ K min^{-1}. The samples were equilibrated for 10 min at 403 K before cooling and for 10 min at 220 K before heating. The sample masses were between 5 and 20 mg. Cooling was performed by a dry ice and ethanol mixture. The sample pans were kept

Table 1 Characterization of P(EO-b-TBMA) diblock copolymers

Sample code	$M_{n,PEO}$[a] (g mol^{-1})	$M_{n,PEO}^{exp}$ (g mol^{-1})	$M_{n,PTBMA}$[a] (g mol^{-1})	$M_{n,total}^{exp}$ (g mol^{-1})	w_{PEO}[a] (wt%)
ah 161	4000	5400[b]	4200	10 000[b]	47.3
a 163	9800	9000[c]	–	–	98.8
ah 163	9800	9000[c]	10 500	13 800[b]	47.7
ah 167	4300	–	16 800	–	19.8
ah 168	8600	–	12 600	26 600[d]	40.0
ah 169	12 700	–	8400	–	59.6
ah 170	17 000	–	4200	–	79.6
ah 171	14 500	–	6600	–	68.3
ah 172	1950	1700[e]	12 600	13 100[c]	12.6
ah 174	21 000	28 900[b]	12 600	–	62.1
ah 175	250	–	12 600	12 200[b]	1.0
ah 176	562	–	12 600	12 400[c]	3.4
ah 191	3000	2800[e]	12 200	–	19.0
ah 192	5000	–	12 600	–	27.7
ah 193	20 100	–	1500	–	92.5

[a] Calculated from the amount of monomer and initiator by correction with conversion including initiator residue
[b] S.e.c. (calibration with PS standards)
[c] Vapour pressure osmometry in toluene solution at 310 K
[d] Membrane osmometry
[e] Hydroxyl group analysis (from reaction with acetic anhydride)

Table 2 Thermal properties of P(EO-b-TBMA) diblock copolymers of constant PTBMA (12 600 g mol^{-1}) and varying PEO block length. $T_{c,max}$ and $T_{m,max}$ are the peak maxima of crystallization and melting peaks, respectively, ΔH_m is the melting enthalpy and α is the crystallinity

Sample code	$M_{n,PEO}$ (g mol^{-1})	$T_{c,max}$ (K)	$T_{c,max}$ (K)	$T_{m,max}$ (K)	l_{lam} (nm)	ΔH_m[a] (J g^{-1})	α[b] (%)
ah 175	250	–	–	–	–	–	–
ah 176	562	–	–	–	–	–	–
ah 172	1950	–	240	311	1.46	13	50
ah 191	3000	291	246	317	1.79	22	58
ah 192	5000	301	–	322	2.28	33	58
ah 168	8600	309	–	328	3.12	46	56
ah 174	21 000	314	–	330	3.72	71	56

[a] Per total sample weight
[b] Reduced to gram PEO using $\alpha = (\Delta H_m / \Delta H_\infty) \times 100\%$ with $\Delta H_\infty = 203$ J g^{-1} (ref. 23)

under a flow of dry nitrogen. The uncertainties in temperatures were estimated to be about 0.3 K.

For small-angle X-ray scattering (SAXS) a Kratky-type camera was used (input slit 60 μm, counter slit 150 μm). The primary radiation (Cu Kα, $\lambda = 0.154$ nm) was monochromatized by total reflection at a glass plate. A NaI scintillation counter was used as the detector. The scattering vector is defined as $h = (4\pi/\lambda) \sin \theta$ for scattering angle 2θ. The interval $h = (0.06-2)$ nm^{-1} was investigated using a step width of $\Delta h = 0.02$ nm^{-1}. The long periods were estimated from the maxima of the Ih^2 function (I is the intensity). Before the investigations, the samples were prepared in d.s.c. in the same manner as for d.s.c. experiments in order to have comparable conditions to d.s.c. experiments. The samples were equilibrated for 10 min at 403 K before cooling and for 10 min at 220 K before heating. The cooling and heating rates were again 10 K min^{-1}. The heating cycle was stopped at 300 K (i.e. heating trace without melting). The sample masses were about 50 mg.

RESULTS AND DISCUSSION

Investigations on the non-equilibrium structure

In this section, the domain structure is described as found after the cooling/heating cycle described in the previous section. First, the dependence of the PEO lamellar size is described as a function of the PEO block length.

In *Table 2* and *Figure 2* it is shown that the shorter the PEO segment length the smaller the crystallization temperatures (and the critical nucleus size) and melting temperatures. The transition from heterogeneous to homogeneous nucleation occurs at a molecular weight of almost 3000 g mol^{-1}. No crystallization can be observed below 2000 g mol^{-1} PEO segment length. That means the domain size is not sufficient to form a critical homogeneous nucleus. Moreover, the crystallinity per gram of PEO remains almost constant (nearly 60%), i.e. in the case of a *high* PTBMA block length and content, the crystallinity is weakly dependent on the PEO block length.
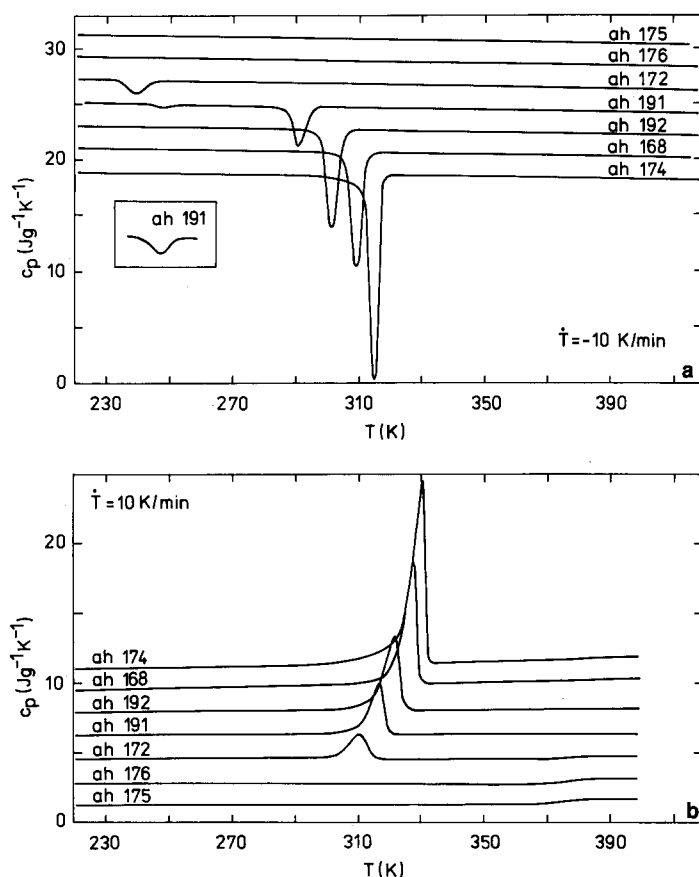
Figure 2 (a) Crystallization and (b) melting behaviour of diblock copolymers of constant PTBMA and varying PEO block length (from ref. 21). The insert of sample ah 191 is stretched by a factor of 10
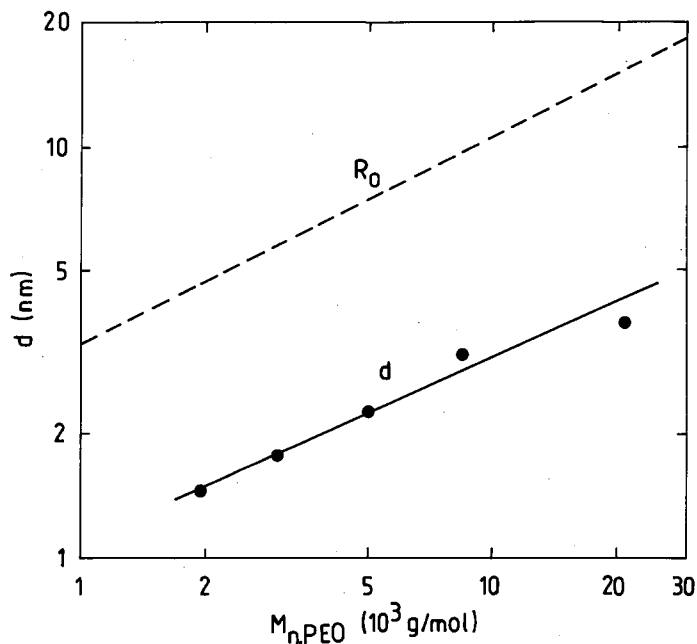

Figure 3 Lamellar thickness d (full line) and estimated PEO molecular radius R_0 (broken line) as a function of PEO molecular weight of the samples of *Figure 2* (R_0 = mean chain end distance)

The lamellar thickness d is shown in *Figure 3* as a function of PEO molecular weight (d was estimated from the melting temperatures by the Thomson formula using $T_m^\infty = 342.7$ K, $\sigma_e = 1.75$ μJ cm^{-2} and $\Delta h_f = 260$ J cm^{-3} (ref. 23)), assuming that σ_e is constant (see also *Table*

2). The size of the molecular radius R_0 is also given for comparison (broken line, $R_0 = 0.7$ nm $\times$ $Z^{1/2}$). It can be seen that the lamellar thickness is approximately proportional to $Z^{1/2}$, and also that the lamellar thickness is smaller than the molecular radius by a factor of 3. Linear regression gives:

$$l_{lam} \sim Z_{EO}^{0.41 \pm 0.05} \tag{5}$$

Using the thermal properties of other P(EO-b-TBMA) block copolymers (see *Table 3*), predictions as to the influence of the block length of the amorphous (PTBMA) chain segment can also be made, if the influence of PEO segments is preserved:

$$l_{lam} = (1 \pm 0.13) \times 1.09 \text{ nm} \times Z_{EO}^{0.41} Z_{TBMA}^{-0.27} \tag{6}$$

(the $\pm$ sign indicates the deviation of a single measurement; the standard deviation is 3.5%), and

$$T_m = T_m^\infty - \frac{42.3 \text{ K}}{Z_{EO}^{0.41} Z_{TBMA}^{-0.27}} \tag{7}$$

where $T_m^\infty = 342.7$ K. The uncertainty of T_m depends on the melting-point depression and is about 3 K at a melting-point depression of 20 K.

Equation (6) conforms with the type of equation given by DiMarzio *et al.*[14] (equation (2)) and Whitmore and Noolandi[18,19] (exponents in these equations are 1 and -0.333 or 1 and -0.417, respectively) for the thickness of crystalline layer in crystalline–amorphous diblock copolymers. For comparison of the exponents, however, one has to take into consideration that the theoretical results are only valid for thermodynamic equilibrium, which cannot be achieved in the experiments. The starting point of crystallization is the (stretched) polymer coil (see also Rault *et al.*[24,25]), and far-reaching diffusion should be necessary even for domain formation, which is additionally hindered by low PTBMA mobility. The state far from equilibrium is indicated by the observation that the melting temperature is dependent on the crystallization temperature (see also *Figure 7* below). Nevertheless, the influence of the degree of polymerization of the PTBMA segment is evident even for non-equilibrium: the lamellar thickness decreases with increasing PTBMA degree of polymerization.

From *Table 3* it is also seen that crystallinity is dependent on the composition of the diblock copolymer; crystallinity decreases with decreasing PEO fractions.

SAXS investigations make assertions on the size of the total repeat length in the periodic morphologic structure of the diblock copolymers possible. As a model for the diblock copolymers considered, a periodic layer structure PEO–PTBMA is assumed. (This model is supported by the fact that, as mentioned above, till now only layer structures have been found for crystalline– amorphous block copolymers[15–17].)

Figure 4a shows the SAXS curves of the block copolymers mentioned in *Table 2*. Three phases should be considered: crystalline PEO, amorphous PEO and PTBMA. We start with the assumption that scattering contributions can be expected mainly from the PEO– PTBMA layer arrangement (and not from the semi-crystalline lamellar structure). This is demonstrated in *Figure 4b*: at a temperature of 358 K, above the PEO melting temperature ($T_m^\infty = 342.7$ K), the same long periods L can be estimated from SAXS as for the low-temperature crystalline state. The maxima in the melt

are not so sharp because the mean electron density is lower there. The second shoulders visible in *Figure 4* are second-order reflections. Furthermore, the long periods (see *Table 4* and *Figure 5*) are related to the total molecular weight according to the following relationship:

$$L \sim M_{\mathrm{n,total}}^{0.58 \pm 0.07} \tag{8}$$

as expected for the (amorphous–amorphous) block copolymer domain structure.

Because of the fact that the densities in the PEO and PTBMA domains cannot be essentially changed by chain stretching, the thickness of these domains can be

calculated using the PEO–PTBMA layer model with the usual densities (results see *Table 4*).

Comparing the domain sizes and the crystalline lamellar thicknesses, the structurization of PEO domains can be estimated, supposing that the crystalline lamellae are parallel to the domain layers (crystal stems perpendicular to the domain layers). The model shown in *Figure 6* can be reconciled best with the experimental results, even if the restrictions regarding the uncertainties of the absolute values of molecular weights are taken into consideration. This means that, in non-equilibrium, the PEO structure in the block copolymer is similar to those

Table 3 Thermal properties of additional P(EO-*b*-TBMA) diblock copolymers

Sample code	$M_{\mathrm{n,PEO}}$ (g mol^{-1})	$M_{\mathrm{n,PTBMA}}$ (g mol^{-1})	$T_{\mathrm{c,max}}$ (K)	$T_{\mathrm{m,max}}$ (K)	l_{lam} (nm)	$\Delta H_{\mathrm{m}}{}^a$ (J g^{-1})	α^b (%)
ah 193	20 100	1500	311	336	6.69	151	79
ah 170	17 000	4200	313	335	5.91	107	66
ah 171	14 500	6600	311	334	5.30	89	64
ah 169	12 700	8400	308	330	3.60	70	58
ah 163	9800	10 500	310	328	3.23	58	59
ah 167	4300	16 800	286	318	1.84	20	49
ah 161	4000	4200	290	318	1.88	48	50

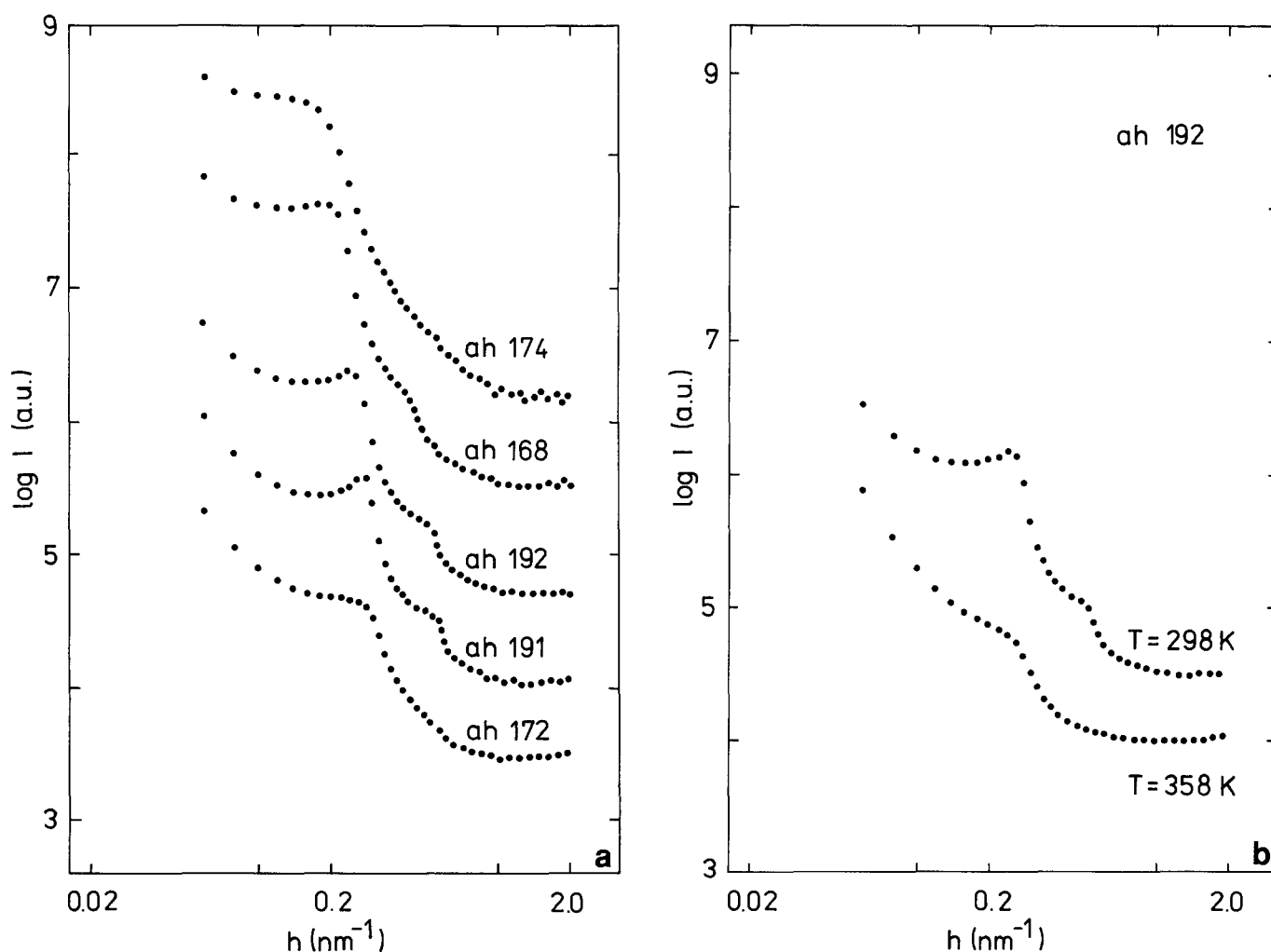^{a,b}See notes in *Table 2*

Figure 4 (a) SAXS results on diblock copolymers of constant PTBMA and varying PEO block length (see also *Tables 2* and *4*). (b) SAXS results on sample ah 192 at room temperature ($L = 23.5$ nm) and above the PEO melting temperature ($L = 22.4$ nm)

Table 4 Structure model parameters of P(EO-*b*-TBMA) diblock copolymers. Φ_{PEO} is the volume fraction of (amorphous) PEO, L is the SAXS long period, d is the domain thickness, l_{lam} is the crystalline lamellar thickness, d_{cr} is the total thickness of crystalline phase in d_{PEO}, α is the crystallinity and N is the (calculated) number of crystalline lamellae per PEO domain

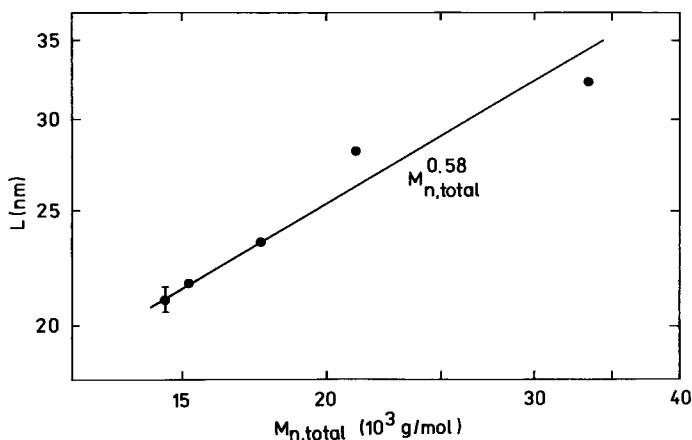| Sample code	Φ_{PEO} (%)	L (nm)	d_{PEO} (nm)	d_{PTBMA} (nm)	α (%)	d_{cr} (nm)	$l_{lam}{}^{a}$ (nm)	N
ah 174	60.2	32.1 ± 0.5	19.3	12.8	56	10.8	3.72	2.91
ah 168	38.3	28.1	10.8	17.3	56	6.05	3.12	1.94
ah 192	26.5	23.5	6.23	17.3	58	3.61	2.28	1.58
ah 191	17.8	21.7	3.86	17.8	58	2.24	1.79	1.25
ah 172	12.3	21.0	2.58	18.4	50	1.29	1.46	0.88

*a*Value taken from *Table 2*

Figure 5 SAXS long periods as a function of the total molecular weight of diblock copolymers; see also *Table 4*
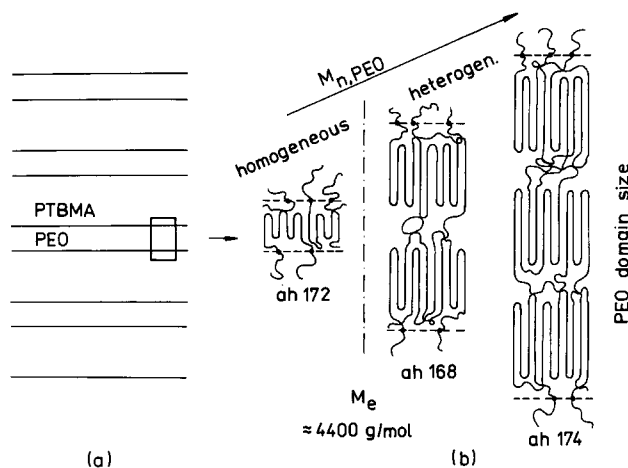

Figure 6 Structure model for P(EO-*b*-TBMA) diblock copolymers: (a) domain layer arrangement; (b) structurization of PEO domain. M_e marks the critical entanglement molecular weight

in homo-PEO. Only the crystalline lamellae are somewhat smaller than for comparable homo-PEOs.

The transition from single-layer to multilayer structure occurs near the critical entanglement molecular weight of PEO (4400 g mol^{-1})[26].

Phase behaviour in thermodynamic equilibrium

Knowledge of the equilibrium melting temperature T_m° would allow an estimation of structure and size of the crystalline domains in equilibrium. We suggest that an

estimate of T_m° can be obtained by extrapolating the crystallization temperature *versus* melting temperature straight line up to the line $T_c = T_m$ (Hoffman– Weeks method[27]). Using the Thomson equation, the size of the crystalline lamella l_{eq} can be estimated from T_m°, and this can be compared with the thickness of the extended-chain crystal l_{max} and the PEO domain thickness d_{PEO}. The values of l_{eq} and l_{max} can be calculated from:

$$l_{eq} = \frac{2\sigma_e T_m^{\infty}}{(T_m^{\infty} - T_m^{\circ})\Delta h_f} \tag{9}$$

and

$$l_{max} = \frac{M_{n,block}}{M_{n,EO}} \times 0.278 \text{ nm} \tag{10}$$

where σ_e is the interfacial tension of the crystal surface; T_m^{∞} is the equilibrium melting temperature of the 'infinitely' thick crystal; Δh_f is the melting enthalpy (J cm^{-3}) for a crystal with 100% crystallinity; $M_{n,block}$ and $M_{n,EO}$ are the molecular weights of the PEO block and the EO monomer unit (44.05 g mol^{-1}), respectively; and 0.278 nm is one-seventh of the unit-cell c axis of the PEO crystal (7/2 helix[28]). The number of folds, n_f, is given by:

$$n_f = l_{max}/l_{eq} - 1 \tag{11}$$

whereas the number of crystalline PEO lamellae per PEO layer, n_{layer}, is given by:

$$n_{layer} = d_{PEO}/l_{eq} \tag{12}$$

assuming a high crystallinity. The absolute values of l_{max}, n_f and n_{layer} contain the uncertainties of absolute molecular weights.
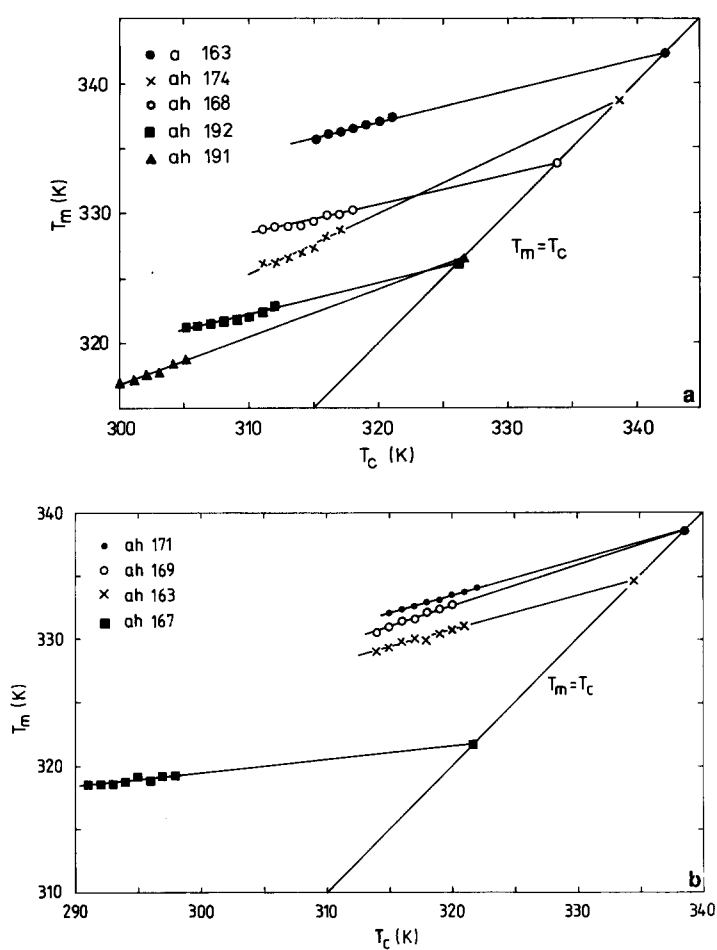
The values of Hoffman–Weeks equilibrium melting temperatures are shown in *Figure 7* and *Tables 5* and *6*. The temperature deviation arises from the deviations of both the slope and the absolute value of the regression line. *Table 5* demonstrates that the larger the PEO block length, the larger the equilibrium melting temperature and the related PEO lamellar and domain thicknesses. Both single-layer and double-layer domain structures are possible; the double-layer structure (samples 2–4 of *Table 5*) can be described as follows:

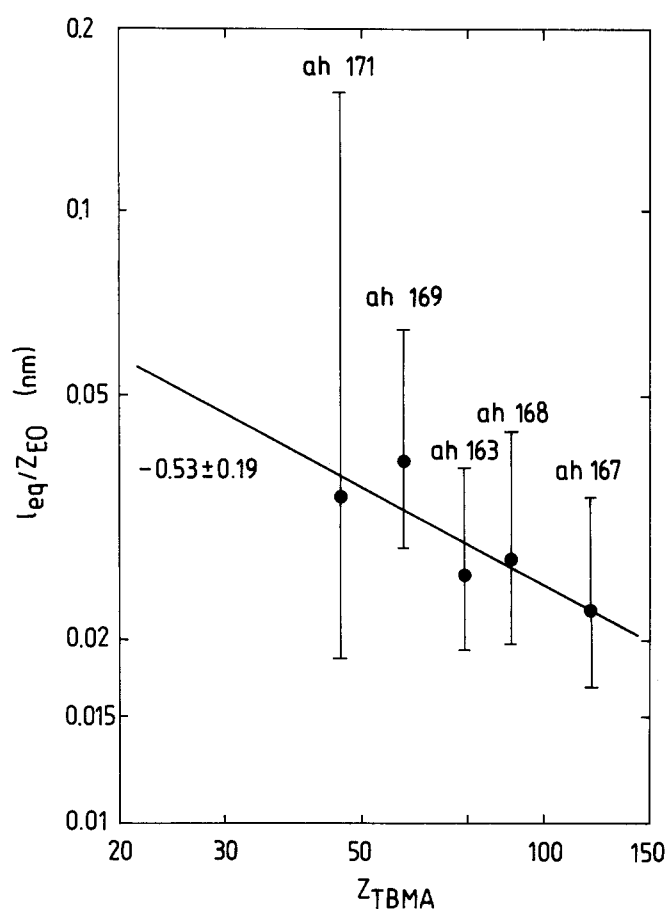$$d_{PEO} \sim l_{eq} \sim Z_{EO}^{0.97 \pm 0.08} \tag{13}$$

A similar relationship should also be found for the single-layer structure, but, of course, the one single measurement value is not sufficient. Using additional diblock copolymers with variable PTBMA block length (see also *Table 6* and *Figure 7b*), the influence of the

Table 5 PEO equilibrium domain structure of P(EO-*b*-TBMA) diblock copolymers of *Table 2* (ΔT from standard deviations). The large *l* deviations (Δl) include the wide extrapolation in *Figure 7*

No.	Sample code	$T_m^\circ \pm \Delta T$ (K)	$l_{eq} \pm \Delta l$ (nm)	l_{max} (nm)	n_f	$d_{PEO}{}^c$ (nm)	$n_1{}^d$
1	a 163	342.2 ± 2.2	92.3 / −75.2	62[a]	0[b]		
2	ah 174	338.7 ± 3.1	11.5 + 39.7/ −5.1	133	10	19.3	1.7
3	ah 168	334.0 ± 3.3	5.3 + 3.2/ −1.5	54	9	10.8	2.0
4	ah 192	326.3 ± 3.5	2.8 + 0.8/ −0.5	32	10	6.2	2.2
5	ah 191	326.6 ± 2.6	2.9 + 0.6/ −0.4	19	6	3.9	1.3

[a] Corresponds to $T_m^\circ = 342.0$ K
[b] Equilibrium (extended-chain crystal)
[c] From *Table 4*
[d] Equal to n_{layer}

Figure 7 Hoffman–Weeks plots (used for extrapolation of the equilibrium melting temperatures) for different diblock copolymers; see also *Tables 5* and *6* (a 163: homo-PEO, $M_n = 9800$ g mol⁻¹)

Table 6 PEO equilibrium domain structure of additional P(EO-*b*-TBMA) diblock copolymers from *Table 3* (ΔT from standard deviations)

No.	Sample code	$T_m \pm \Delta T$ (K)	$l_{eq} \pm \Delta l$ (nm)	l_{max} (nm)	n_f
6	ah 167	321.7 ± 7.2	2.2 + 1.1/ −0.6	27	12
7	ah 168[a]	334.0 ± 3.3	5.3 + 3.2/ −1.5	54	9
8	ah 163	334.6 ± 2.7	5.7 + 2.8/ −1.4	62	10
9	ah 169	338.6 ± 1.6	11.2 + 7.2/ −3.2	80	6
10	ah 171	338.6 ± 3.2	11.2 + 40.0/ −4.9	92	7

[a] From *Table 5*. Sample is listed again for the purpose of comparison

Figure 8 Influence of the PTBMA block length on the PEO crystal-lamella thickness

degree of polymerization of the amorphous component can be estimated:

$$d_{PEO} \sim l_{eq} \sim Z_{EO}^{0.97 \pm 0.08} Z_{TBMA}^{-(0.53 \pm 0.19)} \quad (14)$$

independent of the choice of single-layer or double-layer model. (The regression line is indicated in *Figure 8*.) The high degree of uncertainty in equation (14) is due to the uncertainty of extrapolation wide enough to obtain an estimate of equilibrium melting temperatures. The higher the equilibrium melting temperature (T_m°) (the smaller the difference $T_m^\infty - T_m^\circ$), the larger the uncertainty of calculated lamellar size. Moreover, only eight copolymer samples could be used. For the calculation of the exponents, only the mean values of the equilibrium melting temperatures, without their deviations, were

Table 7 Melting temperatures, lamellar thicknesses and long periods of sample ah 174 as a function of annealing time (at room temperature)

Annealing time (days)	T_m (K)	l_{lam} (nm)	L (nm)
0	330.0	3.7	32.1
180	335.1	6.1	32.1
∞	338.7^a	11.5	–

^{a} From Hoffman–Weeks plot (see *Table 5*)

taken into account. The 3σ confidence interval for the exponent -0.53 is from $+0.04$ to -1.10.

Nevertheless, within the bounds of uncertainties, conformity with the theoretical predictions can be established (see equation (2) (DiMarzio *et al.*[14]) and equation (3) (Whitmore and Noolandi[18,19]): exponents 1 and -0.333, and 1 and -0.417, respectively).

The number of folds obtained demonstrates that in thermodynamic equilibrium—in contrast to homo-polymers—folded crystals do exist. The number of folds in the case of a double-layer structure is, of course, greater than in the case of a single-layer structure. However, it can be seen from *Table 5* that the number of chain folds is almost independent of the molecular weight of the PEO segment. The number of chain folds (see *Table 6*) tends to decrease with decreasing PTBMA block length. We observe similar values of n_f as found by Gervais and Gallot[16,17], but they are larger than those predicted by Whitmore and Noolandi (nearly 2), who argued with insufficient knowledge of the chain folding energy.

Comparison of thermal behaviour between P(EO-*b*-TBMA) and P(TBMA-*b*-EO) diblock copolymers (note the different polymerization succession) shows that for the former diblock copolymers a much stronger crystallization hindrance was observed. The reason is that the former PEO block ends with the cumyl potassium initiator group, which strongly hinders the crystal thickening. A similar influence is known from the crystallization of homo-PEO (for instance, Kovacs *et al.*[29] in PEO closed by a diphenyl group). A similar investigation on P(EO-*b*-TBMA-*b*-EO) triblock co-polymers shows an equilibrium structure with only one fold of PEO crystal lamellae[30].

The transition from the non-equilibrium thickness (according to equation (6): lamellar thickness of order of $Z^{1/2}$ based on short-range movements) to the equilibrium thickness (according to equation (14): proportional to Z) demands a larger crystal-lamella thickening for larger PEO block length.

Long-term experiments on sample ah 174 at room temperature show the tendency to larger lamella thickness, whereas the domain size remains constant (see *Table 7*).

CONCLUSIONS

In both non-equilibrium and equilibrium, the crystal-lamella thickness is defined by the degrees of polymerization of both the crystallizable and amorphous blocks. Increasing degree of polymerization of the crystallizable (amorphous) segment leads to increasing (decreasing) crystal-lamella thickness.

The starting point of crystallization is the polymer coil, so that the non-equilibrium dimensions are almost proportional to $Z^{1/2}$ (see ref. 24). The structure in the crystallizable domain is similar to that of homopolymers,

but the crystal lamellae are smaller in the case of block copolymers.

The extrapolated findings for the equilibrium dimensions confirm the theoretical predictions of DiMarzio *et al.*[14] and Whitmore and Noolandi[18,19] within the bounds of experimental uncertainties. A decision in favour of one of the two theories cannot be made. According to these theories, the main reason for the influence of the degree of polymerization of the amorphous component on lamellar crystal thickness is that chain stretching in order to achieve a homogeneous amorphous density is the smaller the larger the amorphous block length. This shifts the free-energy optimum of the total system to smaller thicknesses of the PEO domain.

For the transition from non-equilibrium to equilibrium structures, far-reaching diffusion movements would be necessary in the PEO domain. A noticeable increase of domain size was not found.

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