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Controlling the morphology of polybutadiene–poly(ethylene oxide) diblock copolymers in bulk and the orientation in thin films by attachment of alkyl side chains

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ABSTRACT

A polybutadiene$_{19}$-*block*-poly(ethylene oxide)$_{94}$ (PB–PEO) has been modified by free-radical additions of 2-ethylhexanethiol, 1-decanethiol, and 1-dodecanethiol separately to the PB block. The block copolymers were characterized by DSC, SAXS, XRD and AFM measurements. Above the melting temperature of PEO, PB–PEO showed hexagonal morphology having PB cylinders in the PEO matrix. The addition of alkyl side chains decreased the volume fraction of PEO and the morphology changed to lamellar for ethylhexyl side chains and to reversed hexagonal morphology with PEO cylinders in the PB/alkyl chain matrix for decyl and dodecyl side chains. Below the melting temperature of PEO, all polymers showed lamellar morphology. In the case of dodecyl side chains, the lamellar morphology oriented perpendicular to the air/film interface and was stable against high temperature annealing.

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1. Introduction

Current research activities on block copolymer morphology focus, among other objectives, on increasing the length scales above the tens of nanometers, achieving long-range ordered morphologies and determining the orientation of the ordered structures. The self-organized morphology of block copolymers can successfully be controlled by varying the total degree of polymerization, N, the Flory–Huggins interaction parameter, χ, and the volume fraction, f, of the components. For conformationally isotropic AB diblock copolymers in the strong segregation limit where $\chi_{AB}N \gg 10$, the morphology changes from disordered to BCC spheres to hexagonal cylinders to lamellar as volume fraction of one component, say f_A, increases from 0 to 0.5 (f_B changes from 1 to 0.5). The morphology changes symmetrically on the other side of the phase diagram when f_A goes from 0.5 to 1 (f_B goes from 0.5 to 0). For a given pair of strongly incompatible components A and B, one way to change the morphology is to increase the degree of polymerization of one block, N_A, while keeping that of the other block, N_B, constant. For components having equal monomer volumes, going from $f_A = 0.25$ ($N_A = n$, $N_B = 3n$; hexagonal morphology) to $f_A = 0.50$ ($N_A = 3n$, $N_B = 3n$; lamellar morphology) require increasing N_A by $2n$. An easier way of changing the composition is the attachment of side chains to the backbone of one component. To go from $f_A = 0.25$ to $f_A = 0.50$, the additional $2n$ monomers must be distributed between the starting $N_A = n$ backbone monomers. This is equivalent to attaching two monomer long side chains to each backbone monomer assuming 100% functionalization. In controlling the morphology, the synthetic route of attaching smaller side chains is much easier than increasing the degree of polymerization of one block due to high viscosities of large molecular weight components. In addition to the change of composition, the attachment of side chains also affects the morphology indirectly by changing the interaction parameter χ_{AB}.

The effect of side chain modifications on the morphology of the block copolymers has been previously investigated in various systems. In a polystyrene-*block*-poly(4-vinyl pyridine) (PS–PVP) copolymer, the detachment of the hydrogen-bonded pentadecylphenol side chains from PVP at high temperatures changed the lamellar morphology to hexagonal where PVP block formed cylinders in the mixture of PS–pentadecylphenol [1]. The increase in the side chain lengths usually stabilizes the structures. In layered mesophases of PS-*b*-fluorocarbon side chains attached PS (or PI), the degree of order of the mesophase increased with the length of the side chains [2]. A counterintuitive case was reported for polystyrene-*block*-poly((ethylene glycol)$_x$ methacrylate)s as a function of side chain length. The order in the lamellar phase decreased with

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number x of ethylene glycol (EG) units, which was attributed to the influence of terminal moiety on the EG side chain [3]. A combined effect of changes in composition and interaction parameter was observed for block–random copolymers consisting of PS and anthracene-functionalized PS. With increasing content of anthracene, a transition from a disordered to a microphase-separated morphology was seen at $\chi N \sim 11$ [4].

1,2-Polybutadiene–poly(ethylene oxide) (PB–PEO) amphiphilic block copolymers are especially important in the studies of block copolymer lyotropic phase behavior because they are dispersable in water [5,6]. The low glass transition temperature of the PB block of about −10 °C makes these copolymers water-dispersable even at a high content of the hydrophobic component. The bulk and thin film morphology and the crystallization behavior of crystalline–amorphous block copolymers for which $T_{ODT} > T_c > T_g$ (where T_{ODT} is the order–disorder transition, T_c is the crystallization temperature of the crystalline block, and T_g is the glass transition temperature of the amorphous block) have recently been reviewed [7,8]. The bulk morphological phase diagrams of the block copolymers above the melting temperature of the crystalline block are similar to those of block copolymers having both amorphous components [6,8]. In the case of strong segregation and amorphous major component, the crystallization of the minor block shows confinement effects [9]. For crystalline major component, the crystallization of the major component significantly affects the resulting morphology below the melting temperature, T_m [10]. In thin films, the orientation of the crystalline lamellae was found to depend on the crystal growth rate [11]. Well-ordered lamellar phases were observed for PB–PEO block copolymers at room temperature down to f_{PB} of 0.13 [5]. The lamellar long period, L, followed a power law dependence $L \sim N^{0.59}$ as a function of degree of polymerization, N, consistent with the prediction of $L \sim N^{2/3}$ in the strong segregation regime [12].

In this work, the effect of alkyl side chains attached to the PB block of PB–PEO diblock copolymers on the self-assembled morphology has been investigated by differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), and scanning force microscopy (SFM). The parent block copolymer (PB_{19}–PEO_{94}; subscripts denote the average numbers of repeating units) was chosen at low hydrophobic content such that it could be increased by the separate free-radical attachment of three different types of alkanethiol side chains: (1) a branched side chain, 2-ethylhexyl thiol, (2) a linear side chain, 1-decanyl thiol, and (3) a longer linear side chain, 1-dodecanyl thiol (see chemical structures in Chart 1) [13].

The codes and corresponding molecular parameters of the polymers investigated in this study are given in Table 1. A PEO homopolymer was used as a reference of crystalline structure in WAXD and SAXS measurements.

Our results show that the morphology of the crystalline–amorphous block copolymers above the melting temperature of crystalline block can be controlled continuously from hexagonal morphology to lamellar morphology to reversed hexagonal morphology by the addition of longer alkyl side chains to the hydrophobic block. In addition, increasing length of alkyl side chains was observed to induce a perpendicular orientation of the lamellar morphology at the air/film interface below the melting temperature of the crystalline block. These results are important in showing the potential of poly(2-alkyl ethylene)-*b*-poly(ethylene oxide) system to achieve the objectives of increasing the length scales of morphology and controlling the orientation of the ordered structures in block copolymer self-organization.

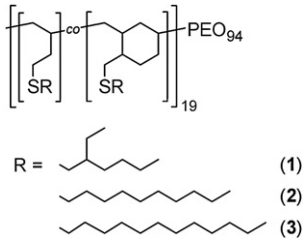

Chart 1. Chemical structures of alkyl-modified PB–PEO block copolymers.

Table 1
Molecular parameters of the polymer samples investigated

Sample ID	Alkyl graft, R	N_{PB}	N_{PEO}	N_R[a]	f_{PEO}[b]
PEO	–	–	113	–	1
PB–PEO	–	19	94	–	0.75
PB/C8–PEO	2-Ethylhexyl	19	94	13	0.51
PB/C10–PEO	Decyl	19	94	15	0.46
PB/C12–PEO	Dodecyl	19	94	14	0.45

[a] Average number of alkyl side chains attached to PB, as determined by elemental analysis.

[b] Densities used for the calculation of volume fractions of PEO: $\rho_{PB} = 0.860$ g/cm^3, $\rho_{decanethiol} = 0.841$ g/cm^3, $\rho_{dodecanethiol} = 0.845$ g/cm^3, $\rho_{ethylhexanethiol} = 0.843$ g/cm^3, $\rho_{PEO} = 1.130$ g/cm^3.

2. Experimental section

2.1. Materials

PB_{19}–PEO_{94} (apparent polydispersity index, PDI = 1.08) was synthesized and modified with alkanethiols (2-ethylhexanethiol → PB/C8–PEO, 1-decanethiol → PB/C10–PEO, and 1-dodecanethiol → PB/C12–PEO) as described earlier [13]. Modified block copolymers did not contain residual double bonds (^{1}H NMR), and the degrees of modification were 71%, 79%, and 72%, respectively (elemental analysis); molecular weight distributions were monomodal (PDI ∼ 1.15; size exclusion chromatography). A PEO homopolymer (Fluka) having molecular weight of 5000 g/mol (degree of polymerization = 113) was used as reference in X-ray scattering measurements.

2.2. Sample preparation

For bulk small-angle X-ray scattering and wide-angle X-ray diffraction measurements, thick films of the polymers were solution cast from toluene solutions, annealed above the melting temperature of PEO (70 °C or 130 °C) for more than 6 h and quenched to room temperature. The samples were then equilibrated in the instrument chamber at the desired temperature prior to measurement. For SFM thin film measurements, the films were spin-coated from 1 wt% solutions in toluene on oxidized silicon substrates. The films were annealed at the desired temperature (70 °C or 130 °C) for at least 2 h and quenched to room temperature.

2.3. Differential scanning calorimetry

The melting and crystallization temperatures of PEO and the side chains in the block copolymers were determined using a Netzsch DSC 200 at 10 K/min heating/cooling rate. After the first heating scan, the DSC data were reproducible in subsequent heating/cooling cycles. The parent PB–PEO was not heated above +150 °C to avoid thermal decomposition.

2.4. Small-angle X-ray scattering

Scattering curves were recorded with a Kratky camera with slit collimation and a rotating anode instrument with pinhole collimation. Measurements with the Kratky camera were performed at 70 °C under vacuum using a proportional counter (Anton Paar, Graz, Austria). Scattering data were recorded in the range of $s = (2/\lambda)\sin\theta = 0.03–0.95\ \mathrm{nm}^{-1}$ (2θ scattering angle, $\lambda = 0.15418$ nm). For the pinhole system, a Nonius rotating anode (4 kW, Cu K_α) and an image-plate detector system were used. With the image plates placed at a distance of 40 cm from the sample, a scattering vector range from 0.05 nm^{-1} to 1.6 nm^{-1} was available. Two dimensional diffraction patterns were transformed into a 1D radial average of the scattering intensity.

2.5. Wide-angle X-ray diffraction

Powder WAXD measurements were done in reflection mode by Nonius diffractometer (Inel, France) using Cu K_α radiation ($\lambda = 0.15418$ nm) and a position sensitive detector. The same samples were used for SAXS and XRD measurements.

2.6. Scanning force microscopy

SFM measurements were performed with a Nanoscope Multimode IIIa microscope (Digital Instruments, Santa Barbara, CA, USA) using silicon cantilevers having $k = 42$ N/m (Nanoworld, Switzerland). Surfaces were scanned at room temperature in tapping mode at a resonance frequency of 200–300 kHz.

3. Results and discussion

3.1. Thermal characterization

The melting and crystallization of PEO blocks were determined by DSC measurements. Fig. 1a shows the heating/cooling DSC scans of PB–PEO taken between 0 °C and +70 °C (thermal decomposition of the sample at higher temperatures, as indicated by less intense and shifted melting and crystallization peaks in subsequent cycles) and of modified PB–PEO block copolymers taken between −50 °C and +300 °C. After the first heating, the subsequent DSC cycles for the copolymers were reproducible without any significant shifts. The melting point of PEO was slightly higher for block copolymers PB/C10–PEO and PB/C12–PEO containing linear C10 and C12 side chains ($T_m \sim +54.5$ °C) as compared to PB/C8–PEO containing branched C8 side chains ($T_m \sim +52.5$ °C). Also, PB/C12–PEO exhibited a slightly lower crystallization temperature ($T_c \sim +23.5$ °C) than PB/C10–PEO and PB/C8–PEO ($T_c \sim +25.5$ °C). For PB/C12–PEO only, side chain crystallization and melting were observed at −23.0 °C and −13.0 °C, respectively. The decrease in the side chain crystallization/melting temperatures with respect to the bulk value of −7.0 °C indicates confinement effects by the crystalline PEO lamellae [14].

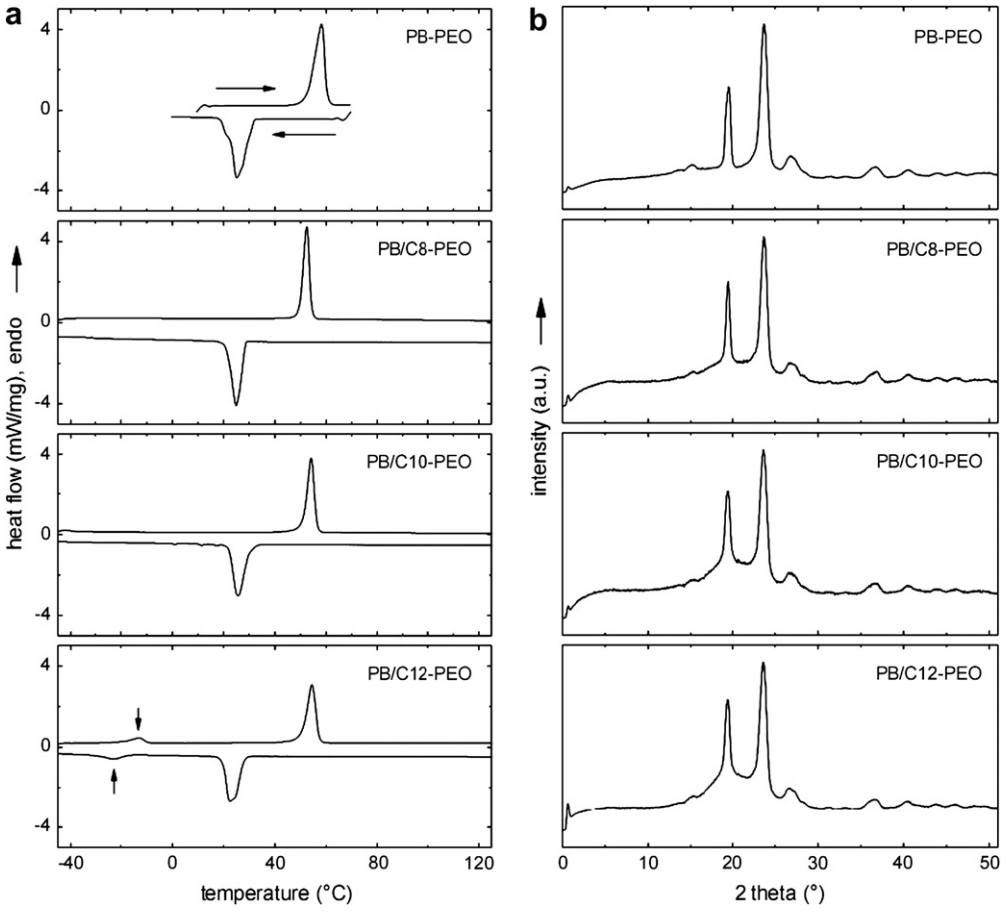

Fig. 1. (a) Second heating and cooling DSC scans for the block copolymers PB–PEO, PB/C8–PEO, PB/C10–PEO, and PB/C12–PEO (top to bottom). Arrows in the bottom panel indicate side chain crystallization and melting (PB/C12–PEO only). (b) Room temperature XRD data of the 70 °C annealed block polymers PB–PEO, PB/C8–PEO, PB/C10–PEO, and PB/C12–PEO (top to bottom).

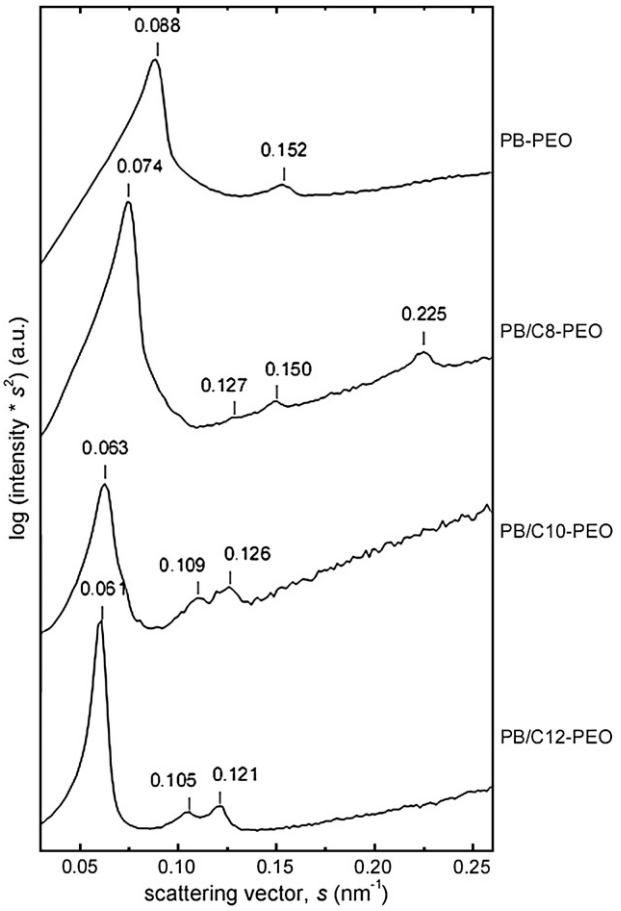

Fig. 2. SAXS curves (Kratky camera) measured for the films of block copolymers PB–PEO, PB/C8–PEO, PB/C10–PEO, and PB/C12–PEO (top to bottom) at 70 °C.

3.2. Structural characterization

The crystalline structure of the PEO did not show any difference for different side chains. Fig. 1b shows the XRD data of the polymers annealed at 70 °C and quenched to room temperature. For all samples, the two most intense peaks were observed at $2\theta = 19.5°$ and 23.6°, respectively.

In the SAXS data (Fig. 2) recorded at 70 °C, that is above the melting temperature of PEO, the first-order reflection for the parent PB–PEO appeared at a scattering vector $s^* = 0.088\ \mathrm{nm}^{-1}$, corresponding to a Bragg spacing of $d = 11.4$ nm. The additional scattering peak at $s = 0.152\ \mathrm{nm}^{-1} = \sqrt{3}s^*$ indicates the presence of hexagonal morphology of cylinders, the distance between the cylinders, L, being 13.2 nm. Considering the calculated volume fractions ($f_{PB} = 0.25$ and $f_{PEO} = 0.75$, see Table 1), the hexagonal morphology consists of PB cylinders in a PEO matrix (Fig. 3a). A measured length of 6.6 nm for PB and PEO implies that both blocks are highly stretched compared to the radius of gyration (R_g). The value of R_g of the PB block is 0.51 nm and that of the PEO block is 1.4 nm. The contour lengths of blocks are 5.4 nm and 33.1 nm, respectively.

PB/C8–PEO, which has 2-ethylhexyl side chains attached to the PB block, adopted a lamellar (Fig. 3b) instead of a hexagonal morphology at 70 °C as confirmed by SAXS (Fig. 2). The first-order scattering peak is located at $s^* = 0.074\ \mathrm{nm}^{-1}$ ($d = 13.5$ nm) and higher-order lamellar peaks are seen at $0.150\ \mathrm{nm}^{-1}$ ($2s^*$) and $0.225\ \mathrm{nm}^{-1}$ ($3s^*$). A transition from hexagonal to lamellar morphology due to the side chain attachment is in agreement with the decrease of the PEO volume fraction from 0.75 in PB–PEO to 0.51 in PB/C8–PEO (Table 1). A very weak peak at $s = 0.127\ \mathrm{nm}^{-1} = \sqrt{3}s^*$ ($L = 15.6$ nm) may correspond to the presence of hexagonal perforated lamellae [10]. Assuming that the PEO block size is about $2R_g$, the upper limit for the length of PB/C8 block at 70 °C should be ~4 nm. Stiffening of the PB backbone and a highly stretched PB/C8 block is expected due to the attached side chains. Because the attached alkyl side chains are above their melting temperatures, they should be randomly oriented around the PB backbone resulting in a "bottle-brush" structure. The attached 2-ethylhexyl side chains to ~70% of PB monomers thus hinder the bending of the PB backbone due to steric repulsion.

Polymers PB/C10–PEO and PB/C12–PEO showed hexagonal morphologies at 70 °C as shown in SAXS data of Fig. 2. For PB/C10–PEO, the first-order reflection appears at a scattering vector $s^* = 0.063\ \mathrm{nm}^{-1}$, corresponding to a Bragg spacing of $d = 15.9$ nm. The additional scattering peaks at $s = 0.109\ \mathrm{nm}^{-1} = \sqrt{3}s^*$ and $s = 0.126\ \mathrm{nm}^{-1} = 2s^*$ confirm the presence of the hexagonal morphology of PEO cylinders in the PB/C10 matrix (Fig. 3c). The distance L between the PEO cylinders is 18.4 nm. For PB/C12–PEO, the first-order reflection appears at a scattering vector $s^* = 0.061\ \mathrm{nm}^{-1}$, corresponding to a Bragg spacing of $d = 16.4$ nm. Similar to PB/C10–PEO SAXS data, additional scattering peaks were also observed for PB/C12–PEO at $s = 0.105\ \mathrm{nm}^{-1} = \sqrt{3}s^*$ and $s = 0.121\ \mathrm{nm}^{-1} = 2s^*$ indicating a hexagonal morphology of PEO cylinders in the PB/C12 matrix (Fig. 3c). The distance L between the PEO cylinders is 19.0 nm. Assuming fully stretched PB/C10 and PB/C12 blocks of length 5.4 nm, the radius of the PEO cylinders is calculated to be 3.8 nm and 4.1 nm, respectively.

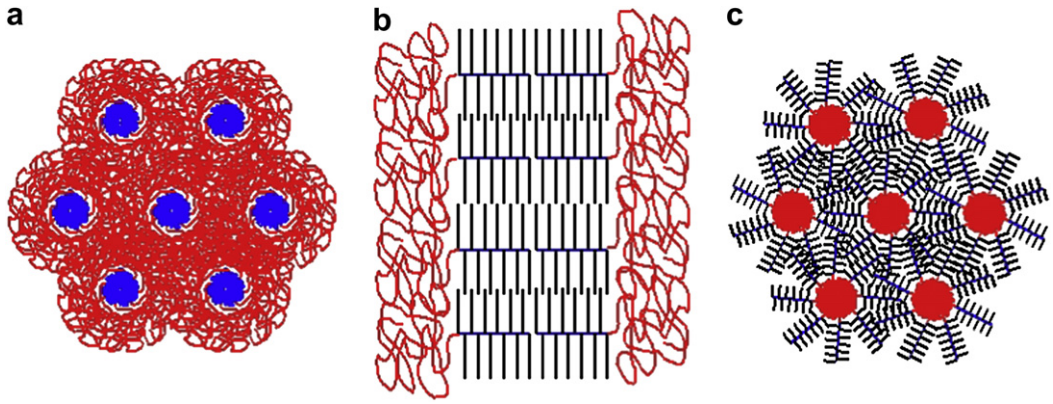

Fig. 3. Illustrations of morphologies observed. (a) PB–PEO: hexagonal morphology of PB cylinders in a PEO matrix. (b) PB/C8–PEO: lamellar morphology. (c) PB/C10–PEO, PB/C12–PEO: hexagonal morphology of PEO cylinders in a PB/C10 or PB/C12 matrix.

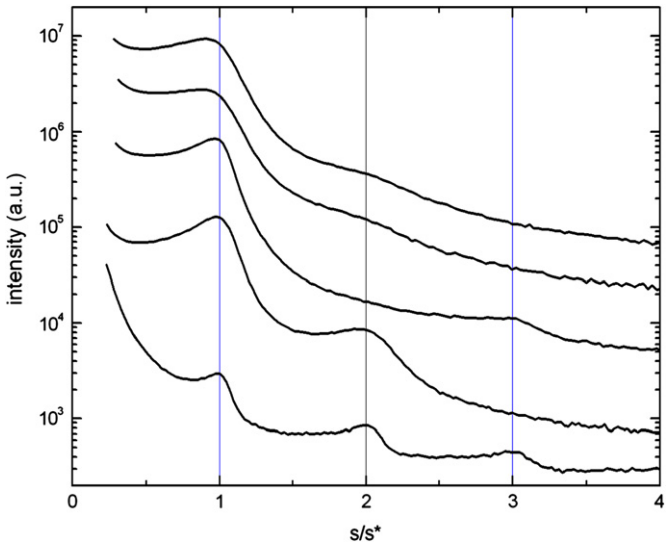

Fig. 4. SAXS data taken at room temperature after 70 °C annealing and quenching to room temperature. From bottom to top: PEO homopolymer, PB–PEO, PB/C8–PEO, PB/C10–PEO, PB/C12–PEO.

Below the melting point of PEO, all samples showed lamellar morphology with integer multiples of s/s^* in SAXS data (Fig. 4). The values of s^* (and d) were 0.072 nm^{-1} (13.8 nm) for PB–PEO, 0.057 nm^{-1} (17.3 nm) for PB/C8–PEO, 0.054 nm^{-1} (18.4 nm) for PB/C10–PEO and PB/C12–PEO.

For PB/C8–PEO, the intensity of the second-order scattering peak is much weaker compared to third order scattering peak. This can be explained by the extinction rule of structural symmetry due to nearly equal layer thicknesses for both the PEO and the PB/C8 lamellae. PEO chains should be folded three or seven times, depending on whether they form interdigitated or bilayered lamellae. Both possibilities are consistent with the cross-sectional area that each block occupies at the interface. Fig. 5a shows the cross-sectional area of the PB/C8 block at the interface. At room temperature, the side chains are molten and orient randomly in all directions perpendicular to the backbone. The dark square at the center represents the PB backbone which is perpendicular to the plane. The segments emanating from the central square represent the side chains pointing randomly in all directions in the plane. For PB/C8, the side chain length corresponds to the length of six all-*trans* C–C bonds (~0.75 nm, see Chart 1); the cross-sectional area of the PB/C8 block is then about 1.5×1.5 nm^2. Fig. 5b shows the cross-sectional area of the PEO crystal structure in the fold-plane [15]. The lines connecting the filled squares represent the chain folds in the plane. The chain axis bends down at filled squares. The dashed line represents the chain folds at the bottom fold-plane. The cut view of the polymer chain along the dashed line is seen in Fig. 5c. An area of 1.3×1.3 nm^2 consists of total of seven folds, four are seen in the top fold-plane and the three in the bottom fold-plane.

For C10 and C12 side chains, a long period of 18.4 nm was measured at room temperature without any indication of structural symmetry. Considering a PB length between 4.3 nm (measured for PB/C8) and 5.4 nm (fully stretched), the PEO thickness should be 7.6–9.8 nm. In the case of bilayers of folded PEO, chains should be folded 6–7 times similar to that observed for PB/C8–PEO. For the parent PB–PEO block copolymer, a long period of 13.8 nm was measured at room temperature. Assuming that the PB block size is ~$2R_g$, the PEO fold length is calculated to be ~5.9 nm, indicating that the PEO chains would be folded five times in a bilayer. The decrease in number of folds is consistent with the available cross-sectional area that PB block occupies at the interface. Under the same preparation and crystallization conditions, the PEO homopolymer exhibiting a contour length of 40 nm showed a first-order SAXS scattering peak at $s^* = 0.066$ nm^{-1} ($d = 15.2$ nm) (bottom curve in Fig. 4), which corresponds to 1–2 folds.

The lamellar morphology formed by the polymers at room temperature could be confirmed by SFM measurements. Fig. 6 shows the SFM phase pictures of the polymers after spin-coating, after annealing at 70 °C for 2 h, and after annealing at 130 °C for 2 h. The corresponding SFM height pictures of the polymers annealed at 70 °C for 2 h are seen in Fig. 7. The PB–PEO sample showed indications of a lamellar morphology after spin-coating, which by annealing improved into ordered lamellae perpendicular to the substrate. The periodicity of the lamellae at room temperature was ~15 nm for both 70 °C and 130 °C annealed films, which is consistent with SAXS measurements. PB/C8–PEO also showed disordered regions of lamellar morphology after spin-coating. A perpendicular orientation of lamellar morphology could not be observed after annealing. The peak-to-peak surface roughness of ~10–20 nm in the height images (Fig. 7) supports parallel orientation of the lamellae with respect to the air/film interface.

Both PB/C10–PEO and PB/C12–PEO showed after spin-coating well-defined lamellar morphologies oriented perpendicular to the substrate. The period of the lamellar morphology in both cases was about 20 nm. PB/C10–PEO films just showed patches of perpendicular alignment after annealing suggesting a transition from perpendicular to parallel orientation of the lamellae. This was also supported by the observation of ~20 nm deep holes in the SFM

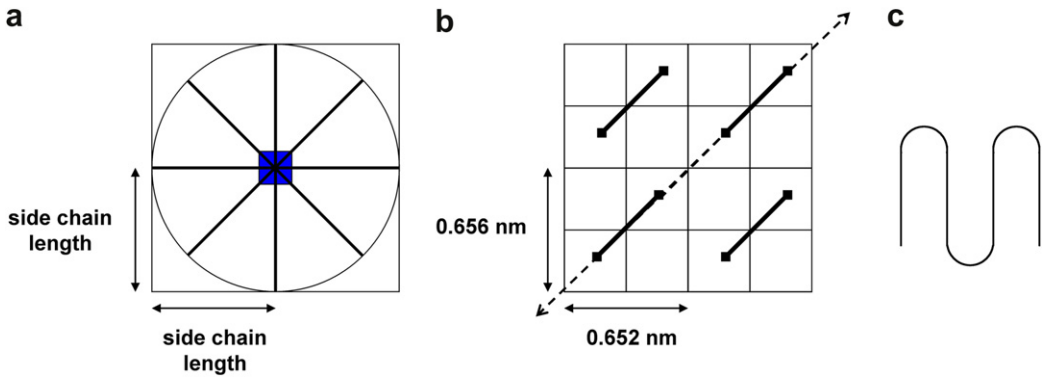

Fig. 5. (a) The cross-sectional area of the PB/C8 block at the interface. The dark square at the center represents the PB backbone which is perpendicular to the plane. The segments emanating from the central square represent the side chains pointing randomly in all directions in the plane. (b) The cross-sectional area of the PEO crystal structure in the fold-plane. The lines connecting the filled squares represent the chain folds in the plane. (c) The cut view of the polymer chain along the dashed line in (b).

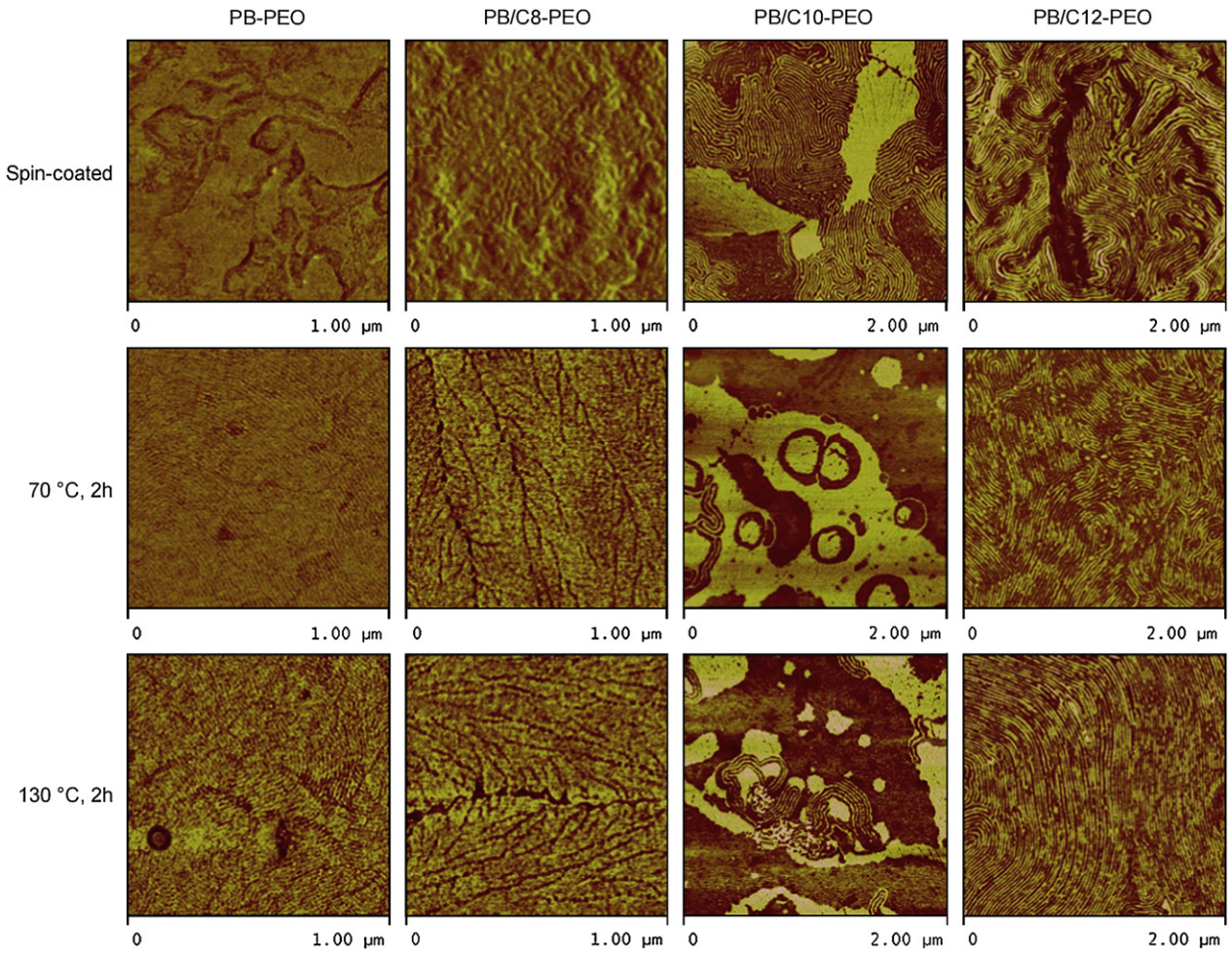

Fig. 6. SFM phase pictures of films of PB–PEO, PB/C8–PEO, PB/C10–PEO, PB/C12–PEO (left to right) after annealing at 70 °C for 2 h, and annealing at 130 °C for 2 h (top to bottom).

height picture (Fig. 7). In contrast, the perpendicularly oriented lamellar morphology of PB/C12–PEO films persisted after annealing with enhanced long-range order and smooth surface topography. The period of the lamellae stayed constant at ~20 nm. A transition in the orientation of the lamellae from parallel orientation to substrate above the melting temperature to perpendicular orientation by crystallization has previously been predicted [11]. This transition is induced kinetically by a decrease in the lamellar spacing for crystal growth rates larger than a critical value. In our case, it is not only the orientation but also the morphology that change by crystallization of PB/C10–PEO and PB/C12–PEO polymers. In isothermal crystallization experiments by DSC, crystallization was slower for PB/C12–PEO compared to PB/C10–PEO and the observation of perpendicular lamellae cannot be attributed to any effect of crystallization rate. Based on the observation of parallel orientation for branched C8 side chains, mixed regions of parallel and perpendicular orientations for C10 side chains and perpendicular orientation for C12 side chains, we concluded that the longer alkyl side chains stabilize the perpendicular orientation of the lamellar morphology at the air/film interface of thin films due to the tendency of the methyl groups of the alkyl side chains to order at the air/film interface. A well-ordered methyl terminated surface at the air/film interface has previously been observed with a comb-shaped copolymer having alkyl side chains [16].

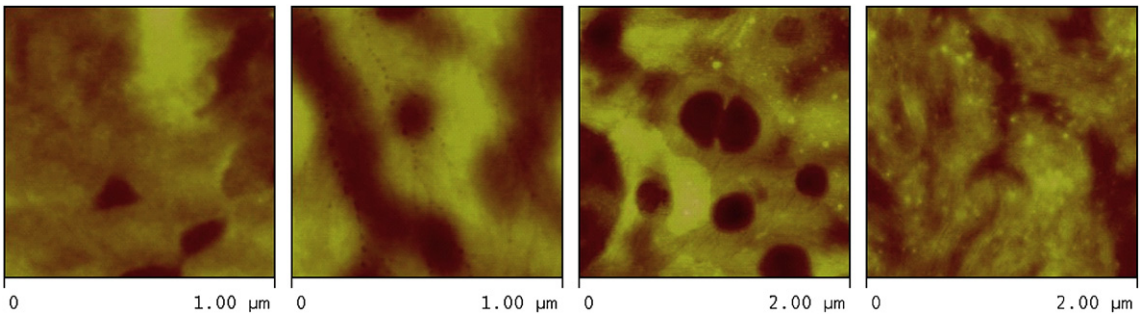

Fig. 7. SFM height pictures of films of PB–PEO, PB/C8–PEO, PB/C10–PEO, PB/C12–PEO (left to right) after annealing at 70 °C for 2 h.

4. Conclusions

A PB_{19}–PEO_{94} diblock copolymer was grafted with three different alkyl side chains (C8: 2-ethylhexyl, C10: dodecyl, C12: dodecyl), and samples were characterized by DSC, SAXS, XRD and AFM. The attachment of alkyl side chains decreased the volume fraction of the PEO block and the morphology changed from hexagonal arrangement for PB–PEO (PB cylinders in PEO matrix), to a lamellar arrangement for PB/C8–PEO, and to an inverse hexagonal arrangement for PB/C10–PEO and PB/C12–PEO (PEO cylinders in PB/C10 or PB/C12 matrix) above the melting temperature of PEO. At room temperature, the structure formation was dominated by the crystallization of PEO and all polymers showed lamellar morphologies. In thin films, the orientation of the lamellae at the air/film interface changed from parallel to perpendicular with longer side chains due to the tendency of methyl groups to order. The perpendicular orientation of the PB/C12–PEO lamellae was stable after several hours of annealing at 130 °C. The results clearly show that the side chain attachment is a simple way to manipulate the composition (and thus the morphology) for the desired application. The alkylated PB–PEO system has the potential to achieve larger periodicities in microphase-separated structures due to stiffening of PB block by side chains and to control the orientation of the ordered structures in thin films. The stable perpendicular orientation of lamellae observed in this system allows the use of these structures as templates in nanolithographic applications.

Acknowledgments

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References

[1] Ruokolainen J, Mäkinen R, Torkkeli M, Mäkela T, Serimaa R, ten Brinke G, et al. Science 1998;280:557.
[2] Andruzzi L, Chiellini E, Galli G, Li X, Kang SH, Ober CK. J Mater Chem 2002;12:1684.
[3] Ishizone T, Han S, Hagiwara M, Yokoyama H. Macromolecules 2006;39:962.
[4] Shenhar R, Sanyal A, Uzun O, Rotello VM. Macromolecules 2004;37:92.
[5] Förster S, Berton B, Hentze HP, Krämer E, Antonietti M, Lindner P. Macromolecules 2001;34:4610.
[6] Deng Y, Young RN, Ryan AJ, Fairclough JPA, Norman AI, Tack RD. Polymer 2002;43:7155.
[7] Sommer JU, Reiter G. Adv Polym Sci 2006;200:1.
[8] Nandan B, Hsu JY, Chen HL. J Macromol Sci Part C Polym Rev 2006;46:143.
[9] Reiter G, Castelein G, Sommer JU, Röttele A, Thurn-Albrecht T. Phys Rev Lett 2001;87:226101.
[10] Lambreva DM, Opitz R, Reiter G, Frederik PM, de Jeu WH. Polymer 2005;46:4868.
[11] Reiter G, Castelein G, Hoerner P, Riess G, Blumen A, Sommer JU. Phys Rev Lett 1999;83:3844.
[12] Semenov AN. Macromolecules 1993;26:6617.
[13] Justynska J, Hordyjewicz Z, Schlaad H. Polymer 2005;46:12057.
[14] Hempel E, Budde H, Höring S, Beiner M. Thermochim Acta 2005;432:254.
[15] Takahashi Y, Tadokoro H. Macromolecules 1973;6:672.
[16] Gautam KS, Dhinojwala A. Macromolecules 2001;34:1137.