7532 *Macromolecules* **2005,** *38,* 7532−7535

Structure Formation of Polystyrene-*block*-poly(γ-benzyl L-glutamate) in Thin Films

Sabine Ludwigs[*,†,⊥] **Georg Krausch,**[†]
Günter Reiter,[‡] **Magdalena Losik,**[§]
Markus Antonietti,[§] **and Helmut Schlaad**[*,§]

Physikalische Chemie II und Bayreuther Zentrum für Kolloide und Grenzflächen, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany; Institut de Chimie des Surfaces et Interfaces, CNRS−UHA, 15 rue Jean Starcky-B.P. 2488, 68057 Mulhouse Cedex, France; and Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Abteilung Kolloidchemie, Am Mühlenberg 1, 14476 Potsdam-Golm, Germany

Received May 25, 2005
Revised Manuscript Received July 11, 2005

The molecular self-assembly of thin block copolymer films is an area of increasing interest, which is due to the inherent beauty of microphase-separated structures and, of course, numerous potential applications.[1−3] Many studies on thin films concern amorphous block copolymer systems, and much fewer deal with block copolymers containing one or more semicrystalline blocks, namely poly(ethylene oxide)s.[4,5] In such systems, the competing ordering processes, i.e., microphase separation and crystallization, lead to a complex hierarchy of structures. It turns out that the true thermal equilibrium state is rarely reached and that the resulting structures are to a large extent determined by the kinetics of ordering processes. This is the molecular basis of processed morphological complexity. The structure formation of copolymers with rigid, interacting segments has—to the very best of our knowledge—not yet been studied in thin films. Rod−coil block copolymers, i.e., block copolymers made of a flexible, amorphous segment and a stiff, rodlike segment, are particularly interesting because of their very rich phase behavior in solution and in the bulk.[6,7]

Important examples of rod−coil block copolymers are those with a synthetic segment and a polypeptide segment, usually referred to as “polypeptide hybrid polymers” or “molecular chimeras”.[8] One of the first and most prominent examples is polystyrene-*block*-poly(γ-benzyl L-glutamate) (PS-*b*-PBLGlu, cf. the chemical structure in Figure 1A).[9] The inherent conformational rigidity of PBLGlu results from an α-helical secondary structure (18/5 helix) due to intramolecular hydrogen-bonding interaction. The spatial orientation of hydrogen bridges gives rise to a permanent dipole moment of 3.5 D per unit,[10] and thus a helix can be regarded as a macrodipole. For a 100% crystalline sample, the contour length of the helix (L) is determined by the product of the projected segment length of a single amino acid unit (= 0.15 nm)[11] times the overall number of units.[12] However, the value of the segment length might be somewhat larger, that is, about 0.17 nm, in solvent-cast films.[13] The diameter of the PBLGlu helix is, as revealed from X-ray analysis of solvent-cast films of PS-*b*-PBLGlu, about 1.6 nm.[14−16]

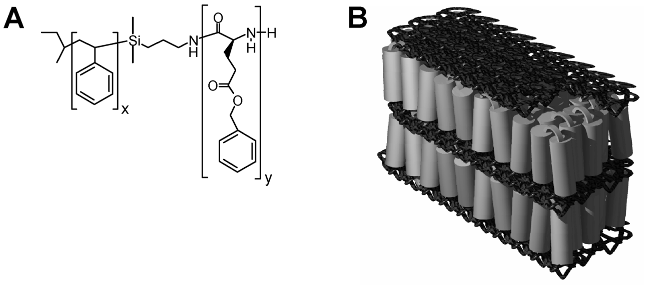

Figure 1. (A) Chemical structure of PS-*b*-PBLGlu. (B) Schematic model of the hexagonal-in-lamellar morphology of PBLGlu-based rod−coil block copolymers (undulations in the thickness of polypeptide layers not shown, see text); helices are represented as rods.

The interactions between the PBLGlu dipoles are considered as the main factor driving PS-*b*-PBLGlu samples of nearly any composition into a lamellar superstructure (Figure 1B).[12] The PBLGlu helices are arranged in antiparallel orientation and packed in a 2D hexagonal array, thus leading to a stiffening of the PBLGlu layers and preferential formation of lamellae. As a matter of the chain length distribution of the helical segment, lamellae are usually not planar but are undulated or zigzagged.[13,16] Interestingly, contradicting the common picture of ideal rodlike molecules, PBLGlu helices are not fully stretched but are folded within the layers, up to seven times depending on the number of BLGlu units.[12,16]

In the following, we will describe the different structures formed by a polystyrene-*block*-poly(γ-benzyl L-glutamate) coil−rod copolymer, PS$_{52}$-*b*-PBLGlu$_{104}$ (Figure 1A, the subscripts denote the number of repeating units), in the bulk and in thin films (thickness: ~3 and 40 nm). As reported earlier for this sample,[16] the amount of BLGlu units in an α-helical conformation is about 90% (circular dichroism spectroscopy). Specimens were made from a solution of the polymer in tetrahydrofuran (THF) either by slowly evaporating the solvent from a thick solution film or by spin-coating. The resulting structures were analyzed by means of small-angle X-ray scattering (SAXS) and scanning force microscopy (SFM) in the Tapping Mode.

Bulk Morphology. A thick film (about 100 μm) of PS$_{52}$-*b*-PBLGlu$_{104}$ was made by slowly drying a semidilute THF solution within 24 h at room temperature and subsequent annealing for 12 h at 60 °C in a vacuum. The main reason for annealing was to completely evaporate the solvent and not to equilibrate the sample. Except for the glass transition of PS ($T_g \sim 70{-}95$ °C, differential scanning calorimetry), the sample exhibits no further thermal phase transition up to 250 °C (decomposition). The SAXS curve (for a description of the experimental setup, see refs 13 and 16) of the powdered sample is shown in Figure 2A. The peaks at scattering vector $s = 0.722$ and 1.295 nm^{-1} with a spacing of $1:1.79 \sim \sqrt{3}$ are consistent with the notion of PBLGlu helices being packed in a hexagonal array. The distance between helices is $d_{\mathrm{H-H}} = 1.60$ nm (= diameter of PBLGlu helices). However, the width of

---

[*] Corresponding authors. E-mail (H.S.): schlaad@mpikg-golm.mpg.de.

[†] Universität Bayreuth.

[‡] CNRS−UHA.

[§] Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Abteilung Kolloidchemie.

[⊥] Present address: Cavendish Laboratory, Department of Physics, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom.

10.1021/ma0510690 CCC: $30.25

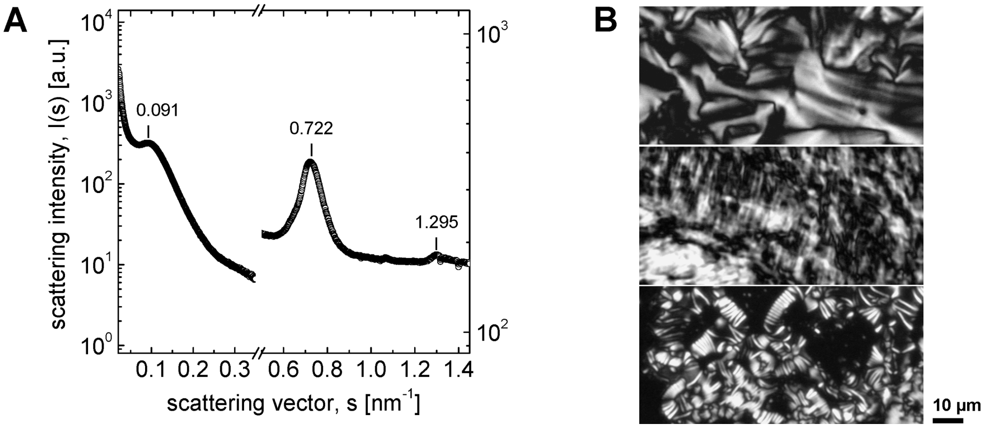

Figure 2. (A) SAXS pattern of the PS$_{52}$-*b*-PBLGlu$_{104}$ film cast from THF solution. (B) Birefringent textures of lyotropic phases of PS$_{52}$-*b*-PBLGlu$_{104}$ in DMA (POM, crossed polarizers).

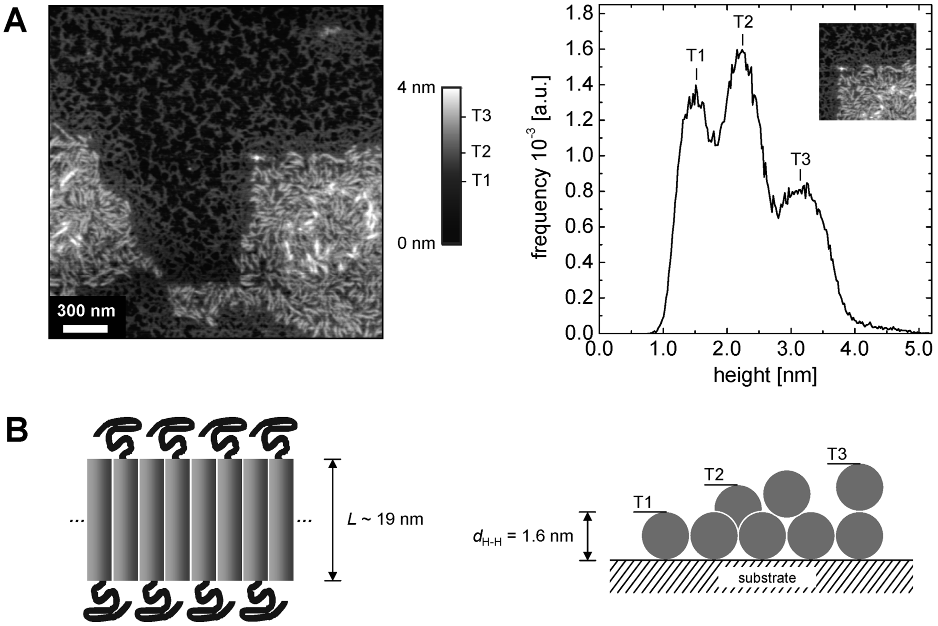

Figure 3. (A) SFM height image and results of histographic analysis of a film of PS$_{52}$-*b*-PBLGlu$_{104}$ obtained by spin-coating from a 0.5 mg/mL THF solution and subsequent exposure to saturated THF vapor for 66 h. (B) Structure model; for details, see text.

the first peak and the low intensity of the second peak indicate that the level of ordering of the helices is rather low. The peak at $s = 0.091$ nm^{-1} emerges from the lamellar superstructure with a long period of $d = 11.0$ nm. Higher-order lamellar reflections are not observed due to undulations in the thickness of PBLGlu layers. Since the long period is smaller than the contour length of the PBLGlu$_{104}$ α-helix ($L \sim 19$ nm),[16] segments must be folded at least once to fit into the layer. Accordingly, the morphology of this film is as depicted in Figure 1B.

Polarization optical microscopy (POM) indicates nematic, smectic, and cholesteric ordering beyond the nanometer length scale for PS$_{52}$-*b*-PBLGlu$_{104}$ in *N*,*N*-dimethylacetamide (DMA); see a selection of three images in Figure 2B.

Thin Films. Films with average thicknesses of about 3 and 40 nm (determined by ellipsometry) were prepared by spin-coating (rotational speed: 2000 rpm) of 0.5 or 5 mg/mL THF solutions of PS$_{52}$-*b*-PBLGlu$_{104}$, respectively, onto polished silicon (100) wafers (Mat. Technologies, Marangis). Wafers were cleaned in a water-saturated UV-ozone atmosphere leading to surfaces with hydrophilic properties. Films were then exposed to a saturated THF atmosphere ("solvent vapor annealing")[17] in a closed chamber at room temperature to remove any nonequilibrium states from the spin-coating process and to allow for a controlled crystallization and long-range ordering. As indicated above, a temperature protocol alone does not allow for an equilibration of the films.

Figure 3A shows the SFM height image of the ~3 nm thick film after the exposure to a saturated THF vapor for 66 h. One can see structural details larger than the average film thickness, which may be best described as randomly oriented rodlike objects being ~20 nm in width and ~100 nm in length. The width of these objects is very similar to the dimension of a single block copolymer molecule ($L \sim 19$ nm). Note that the molecules should be aligned parallel to the surface due to the nematic dipole−dipole interactions between the PBLGlu helices and the substrate.[18] Accordingly, objects should be short "ribbons" made of interdigitated polymer molecules as illustrated in Figure 3B (left), thus compensating the dipoles in a favorable way. This model suggests that PBLGlu helices are fully stretched and do not fold, in contrast to what has been found for the 3D bulk structure.

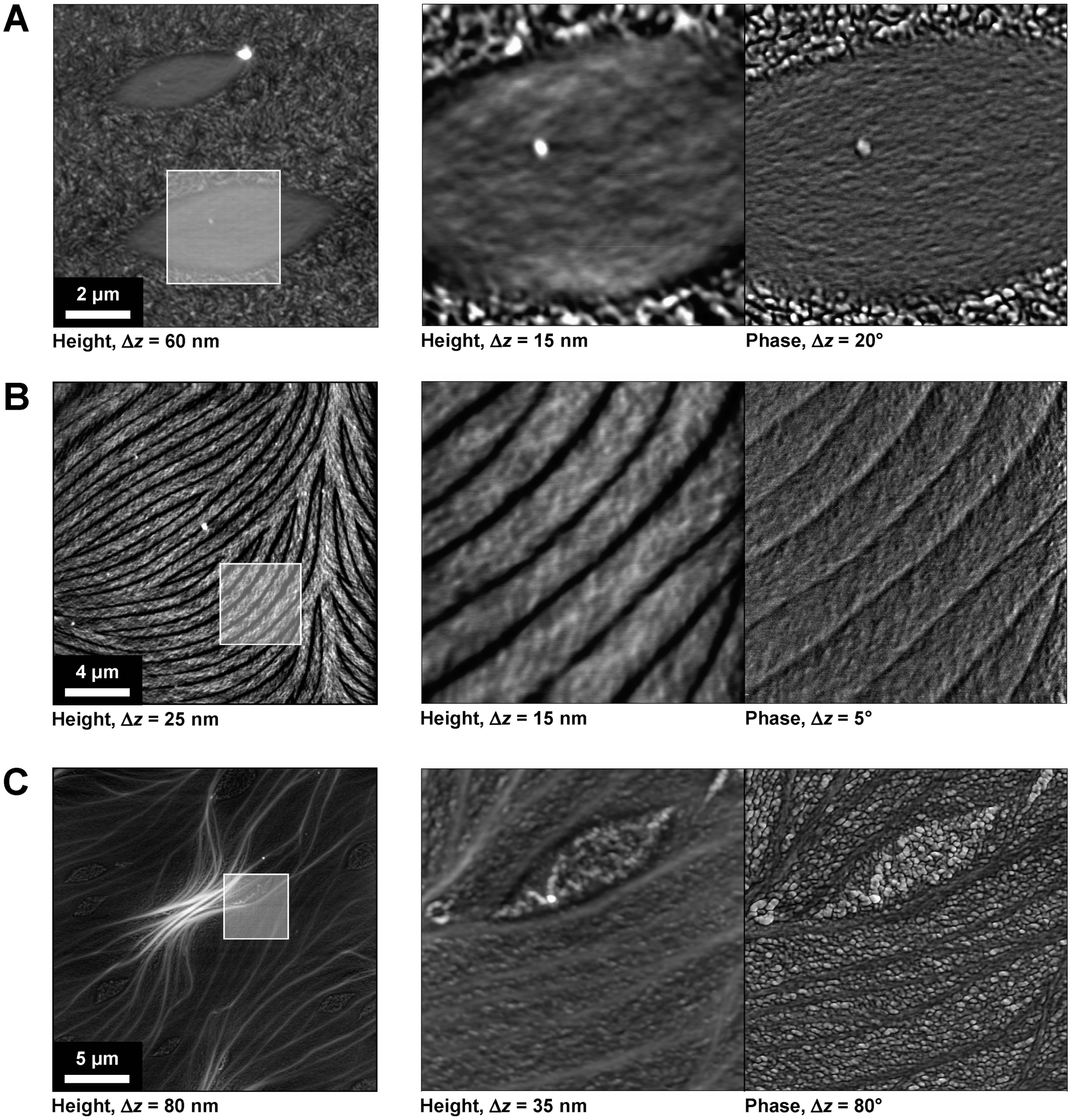

Figure 4. Left: SFM height images of a film of PS_{52}-*b*-$PBLGlu_{104}$ obtained by spin-coating from a 5 mg/mL THF solution and subsequent exposure to saturated THF vapor for 3.5 (A), 22.5 (B), and 42 h (C). Right: SFM height and phase images at higher resolution of the areas highlighted in the pictures on the left (A: 3.5 × 3.5 μm^2; B and C: 5.0 × 5.0 μm^2) (images in C taken from a different region with a similar pattern).

The surface of the film is not smooth but shows characteristic regions or terraces (T1−T3) of distinct heights, $h = 1.5 \pm 0.2$, 2.2 ± 0.3, and 3.1 ± 0.4 nm (see the histogram in Figure 3A). The height of T1 corresponds to the diameter of a PBLGlu helix ($d_{\mathrm{H-H}} = 1.6$ nm). T1 is therefore considered as a (complete) monolayer of polymer molecules being adsorbed to the substrate (see Figure 3B (right)). Stacking of the aforementioned ribbons on top of the first layer results in the formation of T3 ($h_{\mathrm{T3}} \approx 2d_{\mathrm{H-H}}$). The appearance of the step T2 between T1 and T3 with an approximate height of one-half the diameter of a PBLGlu helix ($\Delta h = h_{\mathrm{T2}} - h_{\mathrm{T1}} \approx 0.7$ nm) indicates that the monolayers are interdigitating, seemingly to a larger extent as one would expect for a close packing of rods ($\Delta h = \sqrt{3}/2d_{\mathrm{H-H}} \approx 1.4$ nm for a “hexagonal” packing).

Right after the fast evaporation of solvent by spin-coating, the ~40 nm thick film exhibits a striated texture with a maximal roughness of about 5 nm (not shown). The height modulations look similar to the nematic ribbons found for the thinner film. It may be possible that this texture resulted from the deposition of small aggregates preformed in concentrated solution. Figure 4 shows the SFM images of the film after being exposed to saturated THF vapor for 3.5, 22.5, and 42 h, respectively.

After 3.5 h, micron-sized lense shaped structures with an aspect ratio of about 2.5 within a disordered phase can be observed (Figure 4A). This structure results most likely from nucleation of the (liquid) crystalline mesophase from a differently ordered state (cf. above). Note that the interior of the lenses is comparatively flat and also shows no viscoelastic contrast in phase angle of the Tapping Mode. Accordingly, lamellae are presumably oriented parallel to the surface, which compares well with previous observations on corresponding bulk films.[19]

The situation is getting even more informative after prolonged exposure to THF vapor of film organization for 22.5 h. Figure 4B depicts a typical polydomain. The overall structure is flat but characterized by rather regular, about 5 nm deep and 250 nm wide furrows with a mutual distance of about 1 μm. We assume that the system, similar to amorphous block copolymers,[20] tries to adopt an integer number of lamellae, and the missing matter, which is necessary to fill up the top lamella, is allocated into regular grain boundaries (which otherwise would not be visible). Such periodically striated patterns are known for cholesteric liquid crystals and are usually attributed to so-called "twist grain boundary" (TGB) phases.[21] In fact, a TGB-like twisted smectic phase has been reported for monodisperse PBLGlu.[22] Accordingly, the present film is ordered on at least three different length scales: the peptide helices are closely packed in a lamellar block copolymer mesophase which in itself is regularly twisted on the length scale of micrometers.

Further annealing with THF vapor then only weakly affects the local structure but induces some long-range correlations (Figure 4C).

In summary, we investigated the formation of hierarchical structures of a PS−PBLGlu block copolymer in thin films. On the smallest length scale, the structure is built of short ribbons or lamellae of interdigitated polymer chains. PBLGlu helices are fully stretched in thin films, in contrast to what has been observed in the 3D organized bulk mesophase. Annealing of the structure in saturated THF vapor leads to ordered structures on the micrometer length scale.

At the present, we have a quite good understanding of the mechanism involved in structure formation of PS−PBLGlu on the length-scale of a few tens of nanometers. A comprehensive picture of the processes involved in the formation of larger superstructures is still lacking because these structures are formed under kinetic control and thus are vastly influenced by the history of the sample and the way of preparation. Current work is focused on the detailed analysis of the operating kinetic processes in crystallizing block copolymer systems.

Acknowledgment. Nicolaus Rehse, Hildegard Kukula, Bernd Smarsly, and Erich C. are gratefully thanked for their contributions to this work. Financial support was given by the Max-Planck-Gesellschaft, Deutsche Forschungsgemeinschaft (SFB 448: "Mesoskopisch strukturierte Verbundsysteme", Teilprojekt A12; SFB 481: "Komplexe Makromolekülsysteme in inneren und äusseren Feldern", Teilprojekt B7) and EU Polynano ("Ordered Polymeric Nanostructures").

References and Notes

(1) Krausch, G. *Mater. Sci. Eng., R* **1995**, *14*, 1−94.

(2) Fasolka, M. J.; Mayes, A. M. *Annu. Rev. Mater. Res.* **2001**, *31*, 323−355.

(3) Huang, E.; Rockford, L.; Russell, T. P. *Nature (London)* **1998**, *395*, 757−758.

(4) Reiter, G.; Sommer, J.-U. *Phys. Rev. Lett.* **1998**, *80*, 3771−3774.

(5) Reiter, G.; Castelein, G.; Hoerner, P.; Riess, G.; Blumen, A.; Sommer, J.-U. *Phys. Rev. Lett.* **1999**, *83*, 3844−3847.

(6) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039−4070.

(7) Lee, M.; Cho, B.-K.; Zin, W.-C. *Chem. Rev.* **2001**, *101*, 3869−3892.

(8) Schlaad, H.; Antonietti, M. *Eur. Phys. J. E* **2003**, *10*, 17−23.

(9) Gallot, B. *Prog. Polym. Sci.* **1996**, *21*, 1035−1088.

(10) Hol, W. G. J.; Vanduijnen, P. T.; Berendsen, H. J. C. *Nature (London)* **1978**, *273*, 443−446.

(11) Stryer, L. *Biochemistry*; W. H. Freeman & Company: New York, 1988.

(12) Douy, A.; Gallot, B. *Polymer* **1982**, *23*, 1039−1044.

(13) Schlaad, H.; Smarsly, B.; Losik, M. *Macromolecules* **2004**, *37*, 2210−2214.

(14) Klok, H.-A.; Langenwalter, J. F.; Lecommandoux, S. *Macromolecules* **2000**, *33*, 7819−7826.

(15) Minich, E. A.; Nowak, A. P.; Deming, T. J.; Pochan, D. J. *Polymer* **2004**, *45*, 1951−1957.

(16) Losik, M.; Kubowicz, S.; Smarsly, B.; Schlaad, H. *Eur. Phys. J. E* **2004**, *15*, 407−411.

(17) Elbs, H.; Drummer, C.; Abetz, V.; Krausch, G. *Macromolecules* **2002**, *35*, 5570−5577.

(18) Sohn, D.; Kitaev, V.; Kumacheva, E. *Langmuir* **1999**, *15*, 1698−1702.

(19) Schlaad, H.; Kukula, H.; Smarsly, B.; Antonietti, M.; Pakula, T. *Polymer* **2002**, *43*, 5321−5328.

(20) Ludwigs, S.; Böker, A.; Voronov, A.; Rehse, N.; Magerle, R.; Krausch, G. *Nat. Mater.* **2003**, *2*, 744−747.

(21) Wenzel, A.; Antonietti, M. *Adv. Mater.* **1997**, *9*, 487−490.

(22) He, S.-J.; Lee, C.; Gido, S. P.; Yu, S. M.; Tirrel, D. A. *Macromolecules* **1998**, *31*, 9387−9389.

MA0510690