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Solid-State Structure of Polystyrene-*block*-poly(γ-benzyl L-glutamate): Helix Folding vs Stretching

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Polypeptide hybrid block copolymers or "molecular chimeras"[1] have drawn much attention in recent years, which is due to their complex self-assembly and phase behavior making available a variety of nonclassical morphologies and hierarchical superstructures.[2−6]

The most thoroughly investigated systems are the homopolymers and block copolymers based on poly(γ-benzyl L-glutamate) (PBLGlu). A number of solid-state modifications have been reported for films of α-helical PBLGlu, the most important ones being the so-called forms *B* and *C*.[7−9] Form *B* has a well-defined crystalline structure with a 3D monoclinic unit cell and is obtained by casting from polar solvents like *N*,*N*-dimethylformamide (DMF) or benzyl alcohol at elevated temperature. In form *C*, which is obtained by film casting from nonpolar solvents like chloroform or 1,2-dichloroethane, the α-helices are packed on a rather irregular pseudohexagonal lattice. The packing feature of these two forms is, however, not altered by thermal annealing.

Coil−rod block copolymers based on, for instance, polystyrene (PS) and PBLGlu are known to form a lamellar superstructure, regardless the volume fractions of components.[10] Within the polypeptide sheets, the PBLGlu helices are oriented orthogonal to the PS−PBLGlu interface and are usually not stretched but folded. A folding of helices has not been reported for PBLGlu homopolymers. However, depending on the casting solvent used, helices are either arranged in a 2D hexagonal array (1,4-dioxane)[10] or a more complex, not yet clearly identified pattern (DMF).[11] Also, the degree of order seems to be lower the higher the polarity of the solvent.[12]

At this point the interesting question arises if not only the packing but also the folding of PBLGlu helices is governed by the casting solvent. Solvent polarity seems not to be the key parameter (1,4-dioxane, dielectric constant $\epsilon = 2.2$; DMF, $\epsilon = 36.7$),[9] but it could be the hydrogen-bonding ability: 1,4-dioxane and DMF are both classified as moderate hydrogen-bonding solvents.[13] Therefore, films of a PS_{52}-*b*-$PBLGlu_{93}$ (volume fraction of PBLGlu: $\phi_{PBLGlu} = 0.76$) were cast from three different nonpolar solvents, namely 1,4-dioxane (→ film **B**), anisole ($\epsilon = 4.3$) (→ film **C**), and 1,1,2,2-tetrachloroethane (TCE, $\epsilon = 7.1$) (→ film **D**). DMF was used in an earlier study for the casting of a film of a PS_{52}-*b*-$PBLGlu_{104}$ (→ film **A**).[11] Like dioxane and DMF, anisole belongs to the class of moderate hydrogen-bonding solvents, whereas TCE is a poor hydrogen-bonding solvent. The Hildebrandt solubility parameters of the solvents are about the same, i.e., $\delta = 19.4−20.5$ $MPa^{-0.5}$ and 24.8 $MPa^{-0.5}$ (DMF),[13] and boiling points are beyond 100 °C.

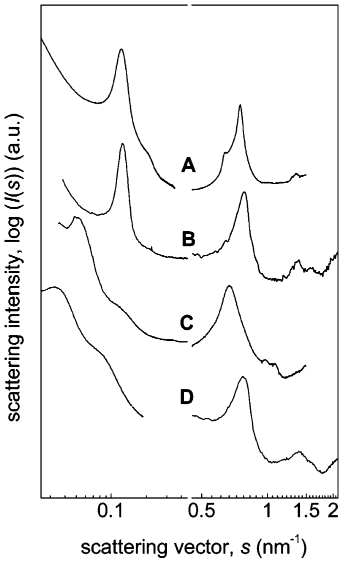

Figure 1. SAXS/WAXS curves of films of PS_{52}-*b*-$PBLGlu_{104}$ cast from DMF solution (**A**)[11] and of PS_{52}-*b*-$PBLGlu_{93}$ cast from 1,4-dioxane (**B**), anisole (**C**), and TCE (**D**).

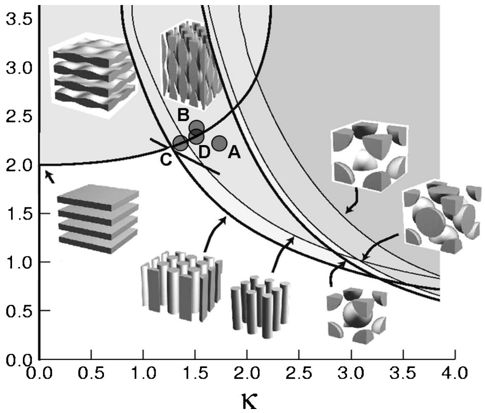

Figure 2. Experimental $\kappa−\iota$ data for the solvent-cast films **A**−**D**, inserted into the generalized phase diagram.

For the preparation of films, 5−10 wt % polymer solutions were placed on a Teflon-coated aluminum foil (BYTAC) and were slowly dried within 24 to 48 h at 40 °C. Specimens were then dried overnight in a vacuum, scratched of the foil, and isolated as powders for analysis with small- and wide-angle X-ray scattering (SAXS/WAXS; experimental details provided elsewhere[11]). The scattering curves obtained, which are shown in Figure 1, were analyzed by applying the $\kappa−\iota$ formalism[14] based on a Porod analysis.[15−18] First, the chord-length distribution, g(r), was determined using the procedure described in ref 16. The Porod's length, l_P, from which then the interface parameter ι was determined, was calculated as the first moment of $g(r)$.[14] Evaluation of the slope of $g(r)$ at very small r yields the curvature parameter κ. It was shown that the κ and ι parameters can be extracted from such transformations of experimental SAXS data into real space.[16] In our case, a Porod law was observed after subtraction of a constant background scattering, which probably originates from 3D density fluctuations.

All four films **A**−**D** were found to exhibit an undulated lamellar morphology, as indicated by the experimental $\kappa−\iota$ data (see Figure 2 and Table 1). As a matter of the fluctuations in

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Table 1. Results of SAXS Analysis of the Solvent-Cast Films PS_{52}-*b*-$PBLGlu_{104}$ (A)[11] and PS_{52}-*b*-$PBLGlu_{93}$ (B−D)

film	solvent	morphology	κ	ι	d_{PS} (nm)	d_{PBLGlu} (nm)
A	DMF	undulated lamellar	1.7	2.2	2	6
B	dioxane	undulated lamellar	1.5	2.4	3	5
C	anisole	undulated lamellar	1.4	2.2	7	12
D	TCE	undulated lamellar	1.5	2.3	10	19

the thickness of layers, just one or two broad Bragg reflections are observed at low scattering vectors ($s = (2/\lambda)\sin\theta < 0.3$ nm^{-1}, 2θ = scattering angle). The packing of the PBLGlu helices is visible at $s > 0.5$ nm^{-1}. For the films **B** and **D**, three peaks with a characteristic Bragg spacing of about $1{:}\sqrt{3}{:}2$ are detected, indicating a hexagonal packing of helices. From the first-order reflection at $s \sim 0.78$ nm^{-1}, the distance between helices is calculated to be $d_{H-H} = 1.5$ nm. In the case of films **A** and **C**, the structure of the PBLGlu domain could not be identified (**A**, peaks at $s \sim 0.64$, 0.75, and 1.35 nm^{-1}; **C**, one broad peak at $s \sim 0.67$ nm^{-1} and two weak peaks at $s \sim 0.98$ and 1.08 nm^{-1}, spacing 1:1.46:1.61).

As can be seen in Table 1 (Figure 1), the nature of the casting solvent has a tremendous effect on the long period (d) of the lamellar structure: $d = 8$ (**A**, **B**), 19 (**C**), and 30 nm (**D**). Although the dimensions are different, the local interface−curvature properties (κ−ι) of all structures are virtually the same, indicating that the films are in an equilibrium state. It is worth noting that the experimental value of κ involves an uncertainty of up to 20%, which is significantly larger than that of ι. The thicknesses of PS and PBLGlu layers were calculated according to $d_{PS} = 0.5l_P/\phi_{PBLGlu}$ and $d_{PBLGlu} = 0.5l_P/(1 - \phi_{PBLGlu})$.[11,15] Accordingly, the thickness of PBLGlu layers is $d_{PBLGlu} = 5$−6 (**A**, **B**), 12 (**C**), and 19 nm (**D**); the error is on the order of 10%. A layer thickness of 19 nm is in good agreement with the estimated contour length of a ~90% α-helical $PBLGlu_{93}$ chain of ~17 nm (see also ref 11). Helices should be fully stretched in film **D** (number of folds: $n = 0$) and otherwise folded once ($n = 1$, **C**), twice ($n = 2$, **A**), or even thrice ($n = 3$, **B**). It is supposed that helices are essentially divided into segments of equal lengths.[10] As an un-folding of helices produces a smaller area per molecule at the PS−PBLGlu interface (see the illustration in Figure 3a), the thickness of PS layers increases from $d_{PS} = 2$ (**A**) to 10 nm (**D**). The plot in Figure 3b suggests that there is an inverse linear dependence between d_{PS} and n.

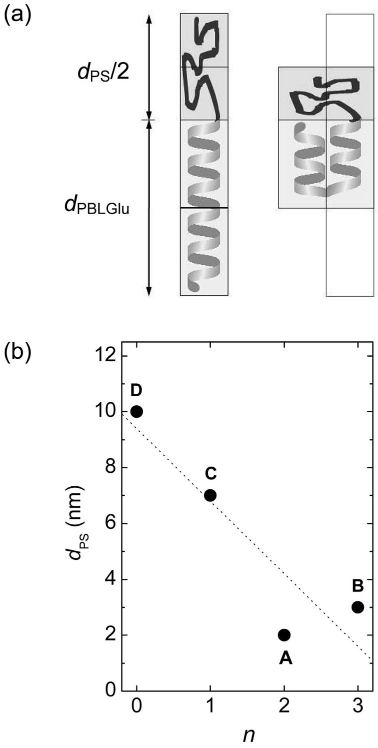

Figure 3. (a) Schematic illustration of the packing of PS-*b*-PBLGlu chains when helices are fully stretched (left) or folded (right). (b) Plot of the thickness of the PS layer (d_{PS}) vs the number of PBLGlu folds (n) as determined experimentally for the films **A**−**D**.

The similar dimensions of lamellae in the films made from DMF and dioxane further support the hypothesis that solvent polarity played a minor or no role in the folding/stretching of helices. Decisive is the capability of the solvent toward hydrogen-bonding interactions. In TCE, the intramolecular hydrogen bonds along the PBLGlu helix should be strongest and thus the tendency toward folding lowest. Hydrogen bonds are weaker in DMF, dioxane or anisole solutions, thus facilitating a folding of helices through dipole−dipole interactions. Regarding the unexpectedly low degree of folding of helices in the anisole-cast film, one might speculate that anisole molecules cannot penetrate the PBLGlu helix because of steric reasons and/or of π−π interactions with the γ-benzyl side groups.

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