Annealing-Induced Changes in Double-Brush Langmuir-Blodgett Films of $\alpha$-Helical Diblock Copolypeptides

Le-Thu T. Nguyen, Andrew J. Musser, Eltjo J. Vorenkamp, Evgeny Polushkin, Gerrit ten Brinke, and Arend J. Schouten*

Department of Polymer Chemistry, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

* Corresponding author. E-mail address: A.J.Schouten@rug.nl.

SUPPORTING INFORMATION

1. Thermal Stability of PLGA-$b$-PMLGSLG.

As shown by the thermal gravimetric analysis (TGA) result in Figure 1, the PLGA-$b$-PMLGSLG diblock copolymer is thermally stable up to 225 °C. Above this temperature, a two-step decomposition process occurs, which is in good agreement with the appearance of two distinct endothermic peaks in the differential scanning calorimetry (DSC) curve at the same range of temperature (Figure 2). From the comparison of the DSC curve of PLGA-$b$-PMLGSLG with those of PLGA and PMLGSLG, the composition process can be assigned to the successive degradation of the PLGA and PMLGSLG blocks, occurring at about 225 and 300 °C, respectively.

In addition, the attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra of PLGA-$b$-PMLGSLG as a function of heating temperature show the conformational change from the $\alpha$-helix to $\beta$-sheet structure starting at ca. 150 °C (Figure 3). Above 220 °C, the decrease in intensity of the C=O
absorption bands and the appearance of absorption bands characteristic of an imide group at 1775 and 1734 cm\(^{-1}\) indicate the thermolysis of the diblock copolymer. Further heating to above 300 °C results in carbonization of the polymer.

Figure 1. TGA thermogram (Perkin-Elmer thermogravimetric analyzer) of PLGA-\(b\)-PMLGSLG (solid line) and its derivative (dashed line), recorded at a heating rate of 10 °C/min under nitrogen. Just before the measurement, the specimen was dried at 40 °C under vacuum for 24 h to remove the moisture.

Figure 2. DSC thermograms (TA instruments DSC 2920) of PLGA-\(b\)-PMLGSLG, in comparison with those of PLGA and PMLGSLG, recorded at a heating rate of 10 °C/min under nitrogen. For clarity the curves are shifted vertically. In order to remove the moisture, the specimens were first scanned up to 120 °C and thereafter cooled to room temperature at 10 °C/min. The results of the subsequent scanning runs are shown in the figure.
Figure 3. ATR-FTIR spectra of PLGA-\textit{b}-PMLGSLG as a function of heating temperature. The samples were heated to the desired temperature at a heating rate of 10 °C/min under nitrogen. For clarity the curves are shifted vertically. ATR FT-IR measurements were carried out on a Bruker IFS88 FT-IR spectrometer equipped with a MCT-A detector, at a resolution of 4 cm\textsuperscript{-1} and with an average of 50 scans.

2. Demonstration of how $\sigma_{01}$ (interface roughness between the silicon substrate and PLGA slab) was adjusted in the fitting process using the two-slab fit model for a XRR curve of the PLGA-\textit{b}-PMLGSLG LB monolayer on the silicon substrate

- Step a: $\sigma_{01}$ was first fixed at 0.48 ± 0.04 nm, the average roughness of bare silicon wafers, and the other parameters were varied until the model adequately simulated the experimental reflectivity. The best curve fit obtained with $\sigma_{01}$ fixed is shown in Figure 4a. $\chi^2 = 0.00731367$.

- Step b: Then $\sigma_{01}$ was adjusted (to 0.74 nm) to obtain a good curve fit (Figure 4b), which reduced $\chi^2$ from 0.00731367 to 0.00534877.

- Step c: After the adjustment of $\sigma_{01}$, further refinement of the other fitted $\rho$ (electron density) and $L$ (layer thickness) parameters for $\chi^2$ minimization to give the final result (Figure 4c) only resulted in slight changes in these parameters by less than 2% of their values.
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Diagram (a) and (b) showing plots of \( R/R_F \) versus 2 Theta (°), with goodness-of-fit statistics \( \chi^2 \) provided for each graph.
Figure 4. Two-slab fits to the XRR curve of the LB monolayer of CoPo\textsubscript{37_24} transferred onto a silicon substrate at 45 mN/m corresponding to (a) step a, (b) step b and (c) step c in the fitting process (see text). The dots represent the experimental data and the full lines represent the fitted curves.