Supporting Information

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Bioinspired All-Polyester Diblock Copolymers Made from Poly(pentadecalactone) and Poly(2-(2-hydroxyethoxy)benzoate): Synthesis and Polymer Film Properties

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![Figure S1](image)

**Figure S1:** $^1$H NMR spectrum of the aromatic homopolymer P2HEB with a benzyl end group (in CDCl$_3$ at 250 MHz). Signals from protons of the benzene ring of the polymer as well as from the benzyl alcohol initiator are located in the region >6.7 ppm. The singlet at 5.29 ppm belongs to the CH$_2$ group from the initiator. The two triplets at 4.56 ppm and 4.26 ppm belong to the CH$_2$-CH$_2$ group in the polymer. Signals of the CH$_2$-CH$_2$-OH end group can also be found at 4.16 ppm and 3.85 ppm. Since this signals had the same integral as the singlet at 5.29 ppm, this proves that each polymer chain bears one benzyl end group and one hydroxyl end group.
Figure S2: FTIR spectrum of the aromatic homopolymer P2HEB: In the area around 3,000 cm⁻¹, C-H stretching bands can be found. Signals from the aromatic group are located above 3,000 cm⁻¹ and signals from aliphatic CH groups can be found below 3,000 cm⁻¹. The strong signal at 1,728 cm⁻¹ can be assigned to C=O stretching bands from the ester groups of the polymer. The C=C stretching bands from the aromatic system are found at 1,600 cm⁻¹. The signals at 1,490 cm⁻¹ and 1,450 cm⁻¹ originate from the =C-H bending vibrations. Another strong signal is the one at 1,301 cm⁻¹, which comes from C-O stretching vibrations of the aromatic ester.

Figure S3: DSC curves of the aromatic homopolymer P2HEB with a benzyl end group with a molecular weight of 28,000 g mol⁻¹.
Figure S4: FTIR spectra of the **PPDL-ester-P2HEB** copolymer synthesized via the macroinitiator approach (black line) and the aliphatic homopolymer **PPDL** (grey line). The newly formed copolyester shows all the characteristic signals from the aliphatic **PPDL** (strong signals from aliphatic C-H stretching vibrations at 2,916 and 2,849 cm\(^{-1}\), strong signal at 1,726 cm\(^{-1}\) characteristic for C=O stretching vibrations of the ester). In addition, new signals characteristic for the aromatic **P2HEB** block appeared (Signals higher than 3,000 cm\(^{-1}\) from CH stretching vibrations from the aromatic ring, signals from the aromatic species at 1,600 cm\(^{-1}\) and 1,301 cm\(^{-1}\), which are assigned to C=C stretching bands from the aromatic system and C-O stretching vibrations).
Figure S5: DSC curves of the block copolymers PPDL-ester-P2HEB with a molecular weight of a) 9,800 g mol⁻¹ and b) 16,000 g mol⁻¹.
Figure S6: FTIR spectra of the block copolymer PPDL<sub>66</sub>-triazole-P2HEB<sub>34</sub> (black line, M<sub>n</sub> = 32,000 g mol<sup>-1</sup>, PDI = 1.43) and the corresponding homopolymers PPDL-alkyne (dark grey line, M<sub>n</sub> = 6,100 g mol<sup>-1</sup>, PDI = 2.45) and P2HEB-azide (light grey line, M<sub>n</sub> = 15,000 g mol<sup>-1</sup>, PDI = 1.24).

Figure S7: DSC curves of the block copolymer PPDL<sub>66</sub>-triazole-P2HEB<sub>34</sub> (M<sub>n</sub> = 32,000 g mol<sup>-1</sup>, PDI = 1.43).
|                  | Height picture | In-Phase | Quadrature |
|------------------|----------------|----------|------------|
| **I. P2HEB**     |                |          |            |
| a) $R_q = 0.3$ nm| ![Image](#)    | ![Image](#) | ![Image](#) |
| **II. PPDL**     |                |          |            |
| a) $R_q = 8.6$ nm| ![Image](#)    | ![Image](#) | ![Image](#) |
|                  | ![Image](#)    | ![Image](#) | ![Image](#) |
| b)               | ![Image](#)    | ![Image](#) | ![Image](#) |
| c)               | ![Image](#)    | ![Image](#) | ![Image](#) |
| **III. Blend**   |                |          |            |
| a) $R_q = 144$ nm| ![Image](#)    | ![Image](#) | ![Image](#) |
### IV. PPDL\textsubscript{21}-triazole-P2HEB\textsubscript{79}

|   | a) $R_q = 3.0$ nm | b) | c) |
|---|------------------|----|----|
| Image 1 | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| Image 2 | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| Image 3 | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |

**Note:** The images depict different scenarios with varying parameters such as $R_q$, color maps, and spatial dimensions.
V. PPDL$_{52}$-triazole-P2HEB$_{48}$

a) $R_q = 5.4 \text{ nm}$

b)

c)

VI. PPDL$_{57}$-triazole-P2HEB$_{43}$

a) $R_q = 3.9 \text{ nm}$

b)
VII. PPDL-66-triazole-P2HEB$_{34}$

a) $R_q = 4.2$ nm

b) 

c)
Figure S8: AFM images of I. P2HEB, II. PPDL, III. a blend consisting of the two homopolymers and IV.-VIII. The block copolymers PPDL-triazole-P2HEB. The subscript after each block represents the molar percentage of each block in the copolymer.
Figure S9: QNM AFM images of a P2HEB layer.

Figure S10: QNM AFM images of a PPDL$_{21}$-triazole-P2HEB$_{79}$ layer.
| Height image | DMT Modulus | logDMT Modulus |
|--------------|-------------|---------------|
| ![Height image](image1.png) 27.0 pm | ![DMT Modulus](image2.png) 33.0 MPa | ![logDMT Modulus](image3.png) 368.0 mPMPa |
| 1.0 µm | 1.0 µm | 1.0 µm |

| Adhesion | Deformation | Dissipation |
|----------|-------------|-------------|
| ![Adhesion](image4.png) 19.0 pN | ![Deformation](image5.png) 3.0 pm | ![Dissipation](image6.png) 17.0 keV |
| 1.0 µm | 1.0 µm | 1.0 µm |

**Figure S11:** QNM AFM images of a PPDL$_{52}$-triazole-P$_{2}$HEB$_{48}$ layer.

| Height image | DMT Modulus | logDMT Modulus |
|--------------|-------------|---------------|
| ![Height image](image7.png) 32.0 pm | ![DMT Modulus](image8.png) 130.0 MPa | ![logDMT Modulus](image9.png) 8.2 log(Pa) |
| 1.0 µm | 1.0 µm | 1.0 µm |

| Adhesion | Deformation | Dissipation |
|----------|-------------|-------------|
| ![Adhesion](image10.png) 6.0 pN | ![Deformation](image11.png) 3.0 pm | ![Dissipation](image12.png) 1.0 keV |
| 1.0 µm | 1.0 µm | 1.0 µm |

**Figure S12:** QNM AFM images of a PPDL$_{66}$-triazole-P$_{2}$HEB$_{34}$ layer.
Table S1: Film properties of P2HEB, PPDL, a 1:1 homopolymer blend, and the PPDL-triazole-P2HEB copolymer series. The subscript after each block represents the molar percentage of each block in the copolymer.

|                   | \( M_n / \text{g mol}^{-1} \) | static CA / ° | advancing CA / ° | receding CA / ° | thickness \(^a\) / nm |
|-------------------|-------------------------------|----------------|------------------|----------------|---------------------|
| PPDL\(^b\)       | 32,000                        | 93 ± 2         | 96 ± 2           | 61 ± 3         | 97 ± 2              |
| P2HEB             | 28,000                        | 85 ± 2         | 88 ± 2           | 56 ± 3         | 135 ± 2             |
| 1:1 Blend         |                               | 89 ± 3         | 95 ± 3           | 60 ± 4         | n.d.                |
| PPDL\(_{21}\)-triazole-P2HEB\(_{79}\) | 30,000                        | 87 ± 2         | 91 ± 2           | 57 ± 3         | 99 ± 2              |
| PPDL\(_{52}\)-triazole-P2HEB\(_{48}\) | 44,000                        | 88 ± 2         | 92 ± 2           | 56 ± 3         | 102 ± 2             |
| PPDL\(_{57}\)-triazole-P2HEB\(_{43}\) | 48,000                        | 89 ± 2         | 92 ± 2           | 59 ± 3         | 103 ± 2             |
| PPDL\(_{66}\)-triazole-P2HEB\(_{34}\) | 32,000                        | 92 ± 2         | 94 ± 2           | 57 ± 3         | 98 ± 2              |
| PPDL\(_{79}\)-triazole-P2HEB\(_{21}\) | 7,900                         | 92 ± 2         | 95 ± 2           | 60 ± 3         | 76 ± 2              |

\(^a\) Film thickness was determined by ellipsometry. \(^b\) Data from \(^{[25]}\)