Supporting Information

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Bioinspired All-Polyester Diblock Copolymers Made from Poly(pentadecalactone) and Poly(3-hydroxycinnamate): Synthesis and Polymer Film Properties

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2. **Figure S2**: FTIR spectrum of the aliphatic homopolymer PPDL.
3.
a)

Figure S3: DSC curves of the aliphatic homopolymers PPDL with a benzyl end group with a molecular mass of a) 2200 g mol\(^{-1}\) and b) 32,000 g mol\(^{-1}\).
4.

Table S1: Polycondensation of 3HCA with various reaction parameters.\textsuperscript{a}

| n(3HCA) / mmol | n(cNaOAc) / mmol | n(Ac\(_2\)O) / mmol | polymerization time / h | \(M_n\) \(^b\) / g mol\(^{-1}\) | PDI \(^b\) |
|----------------|------------------|---------------------|-------------------------|-----------------|---------|
| 6.10           | 0.06             | 52.9                | 5                       | 3000            | 2.10    |
| 9.14           | 0.09             | 52.9                | 6                       | 2900            | 3.20    |
| 60.9           | 0.61             | 211                 | 6                       | 2700            | 1.85    |
| 9.76           | 0.10             | 52.9                | 8                       | n.d.\(^c\)      | n.d.\(^c\) |
| 9.14           | 0.09             | 52.9                | 18                      | n.d.\(^c\)      | n.d.\(^c\) |

\(^a\) Reactions were performed with varying polymerization times in vacuo at 210°C to a full conversion of the monomer. \(^b\) The number-average molecular mass \(M_n\) and the polydispersity index (PDI) were determined by GPC in chloroform using polystyrene standards. \(^c\) The resulting polymer was not soluble in chloroform due to cross-linking.

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Figure S4: \(^1\)H NMR spectrum (CDCl\(_3\), 250 MHz) of the aromatic homopolymer P3HCA.
Figure S5: FTIR spectrum of the aromatic homopolymer P3HCA.

Figure S6: DSC heating curve of the aromatic homopolymer P3HCA.
8.

Table S2: Structures of P3HCA species with different end groups.

| Hydroxyl                  | Acetyl                  | Phenyl                  |     |
|---------------------------|-------------------------|-------------------------|-----|
| ![Hydroxyl-P3HCA-acid](image) | ![Acetyl-P3HCA-acid](image) | ![Phenyl-P3HCA-acid](image) | Acid |
| ![Hydroxyl-P3HCA-anhydride](image) | ![Acetyl-P3HCA-anhydride](image) | ![Phenyl-P3HCA-anhydride](image) | Anhydride |

9.

Figure S7: $^1$H NMR spectrum (CDCl$_3$, 250 MHz) of reaction products of the sequential approach.
Figure S8: FTIR spectrum of reaction products of the sequential approach (black line), the aliphatic homopolymer PPDL (grey line) and aromatic homopolymer P3HCA (light grey line).

Figure S9: GPC elugram of the reaction product of the sequential approach. Higher elution volume signal corresponds to the higher molecular weight PPDL homopolymer and the lower elution volume signals correspond to the newly formed P3HCA homopolymer.
12. 

**Table S3**: Structures of the azide-functionalized P3HCA species with different end groups.

| Hydroxyl          | Acetyl          | Phenyl          | Azide          |
|-------------------|-----------------|-----------------|----------------|
| ![Hydroxyl-P3HCA-azide](image1) | ![Acetyl-P3HCA-azide](image2) | ![Phenyl-P3HCA-azide](image3) | ![Azide](image4) |

13. 

**Figure S10**: FTIR spectra of the block copolymer **PPDL-triazole-P3HCA** (black line) and the corresponding homopolymers **PPDL-alkyne** (grey line) and **P3HCA-azide** (light grey line).
14. Figure S11: DSC curves of the block copolymer PPDL-triazole-P3HCA.

15. Figure S12: AFM height, in-phase and quadrature images of I. P3HCA, II. PPDL, III. A 1:1 blend of the two homopolymers, and IV. PPDL-triazole-P3HCA.

|        | Height image | In-phase image | Quadrature image |
|--------|--------------|----------------|-----------------|
| I. P3HCA<sub>2700</sub> | a) \( R_q = 0.313 \text{ nm} \) | ![In-phase image](image1) | ![Quadrature image](image2) |
| II. PPDL<sub>32000</sub> | a) \( R_q = 8.57 \text{ nm} \) | ![In-phase image](image3) | ![Quadrature image](image4) |
| III. Blend | a) $R_q = 32.3$ nm | b) $R_q = 32.2$ nm |
|-----------|---------------------|---------------------|
| ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |

| III. Blend |
|-----------|
| b) $R_q = 8.83$ nm |
| ![Image](image10.png) |
| c) $R_q = 4.57$ nm |
| ![Image](image11.png) | ![Image](image12.png) | ![Image](image13.png) |
| IV. PPDL-triazole-P3HCA<sub>11700</sub> | a) $R_q = 2.78$ nm |
|----------------------------------------|------------------|
| ![Image](image1.png)                   | ![Image](image2.png) | ![Image](image3.png) |
| b) $R_q = 3.00$ nm                     |
| ![Image](image4.png)                   | ![Image](image5.png) | ![Image](image6.png) |
| c) $R_q = 1.83$ nm                     |
| ![Image](image7.png)                   | ![Image](image8.png) | ![Image](image9.png) |

**Figure S12**: AFM height, in-phase and quadrature images of I. P3HCA, II. PPDL, III. A 1:1 blend of the two homopolymers, and IV. PPDL-triazole-P3HCA.
16.

| P3HCA<sub>2700</sub> |  |
|------------------------|-------------------------|
| height image           | DMT Modulus             | logDMT Modulus          |
| ![Image](image1.png)   | ![Image](image2.png)    | ![Image](image3.png)    |

**Figure S13:** QNM-AFM images of a P3HCA layer.

17.

| PPDL<sub>32000</sub> |  |
|-----------------------|-------------------------|
| height image          | DMT Modulus             | logDMT Modulus          |
| ![Image](image4.png)  | ![Image](image5.png)    | ![Image](image6.png)    |

**Figure S14:** QNM-AFM images of a PPDL layer.
Figure S15: QNM-AFM images of a PPDL-triazole-P3HCA layer.