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Supporting Information

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Synthesis and Self-Assembly of Rod-Rod Hybrid Poly(g-benzyl-L-glutamate)-co-Poly(isocyanide) Block Copolymers**

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General methods and materials

All solvents and chemicals were from Sigma-Aldrich and of the highest purity. The N-carboxyanhydride derivatives of amino acids were synthesized as described by Poché *et al.*[1] LIAA was prepared as described by Cornelissen *et al.*[2] bpyNi(COD) was freshly synthesized according to literature procedures.[3] The polymerizations were performed in a glove-box filled with argon.

Characterization

GPC analysis of the polymers was carried out using a Resipore column (Polymer Laboratories) and a refractive index detector on a Shimadzu GPC system. Solvents used were THF at 30 °C or 0.1 M LiBr in DMF at 60°C. The molecular weight was calibrated using the universal calibration method and polystyrene standards. Proton nuclear magnetic resonance (^{1}H-NMR) were recorded with a Bruker AV-400 (400 MHz) if not stated otherwise. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (0.0). FT-IR spectra were recorded on a BIORAD FTS-60A instrument equipped with a deuterated-triglycine-sulfate (DTGS) detector at a resolution of 2 cm^{-1}. An undersampling ratio (UDR) of 2, an aperture of 2 cm^{-1} at 2000 cm^{-1} were used. The sensitivity was varied between 2 and 8 in a way the output voltage of the detector was as high as possible, but below 10 V. The compounds were dried up from solution onto an ATR ZnSe crystal. A blank ATR ZnSe crystal was used as background. FT-IR data are reported in cm^{-1}. CD spectra were recorded with a Jobin-Yvon CD6 spectrometer. Polarizing optical microscopy images were taken with a Leica DMRB microscope. Confocal laser scanning images were taken with a Leica CLSM. UV spectra of the polymer-nickel complex were measured under an inert atmosphere with a Varian UV spectrophotometer. AFM-imaging was carried out on a nanoscope III from Digital Instruments operating in the tapping mode at room temperature. Samples were prepared by spin coating (1800 rpm) a 1 mg/L polymer solution on freshly cleaved mica.

Block copolymer synthesis

Amino acid-NCA was dissolved in DMF (5 wt%) and an appropriate amount of Ni(COD)(bipyridine) in THF (~40mM) was added. After 24h of stirring at room temperature, the isocyanide monomer was added and stirred again for 24h. The reaction was quenched by the addition of 200 ml of methanol containing HCl (1 mM) causing precipitation of the block copolymer. The block copolymer was dried in vacuo to give a orange-red solid with yields varying between 50-80%. PBLG-PMBI was further purified by another methanol washing step to remove impurities. No PBLG could be detected by GPC (THF). While the polymerization of L,L-IAA is very fast an additional purification step was required to remove non-reacted PBLG. PBLG-b-L,L-PIAA was purified by a washing step with 100 ml of a non-solvent for the block copolymer (e.g. THF) to remove any residual PBLG.

Poly(benzyl-L-glutamate)-b-Poly((*S*)-(-)-a -Methylbenzylisocyanide) PBLG-PMBI. ^{1}H-NMR (δ ppm, CD_2Cl_2, 300 MHz): 8.37 (br, 1H, NH), 7.27 (br, 5H, Phe), 6.87 (br, 5H, Phe), 5.12 (s, 2H, CH_2), 3.97 (s, 1H, CH), 2.63 (b, 1H, CH), 2.31-2.15 (b, 2H, CH2), 1.8 (b, 2H, CH2), 0.8 (b, 3H, CH3). ATR-FTIR (cm^{-1}): 3294.1 (NH), 1734.1 (COO), 1652.0 (Amide I), 1626.5 (C=N), 1547.8 (Amide II). CD: see Figure S2.

Poly(benzyl-L-glutamate)-b-Poly(L-isocyanoalanyl-L-alanine methyl ester) PBLG-PIAA. ^{1}H-NMR (δ ppm, CD_2Cl_2, 300 MHz): 9.45 (br, 1H, NH), 9.18 (br, 1H, NH), 8.37 (br, 1H, NH), 7.29 (br, 5H, Phe), 5.05 (br, 2H, CH_2) 5.4 - 4.0 (br, 2H, CH), 3.63 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 1.8 - 1.1 (br, 6H, CH_3). ATR-FTIR (cm^{-1}): 3270.5 (NH), 1734.1 (COO), 1654.0 (Amide I), 1630.3 (C=N), 1547.8 (Amide II). CD: see Figure S3.

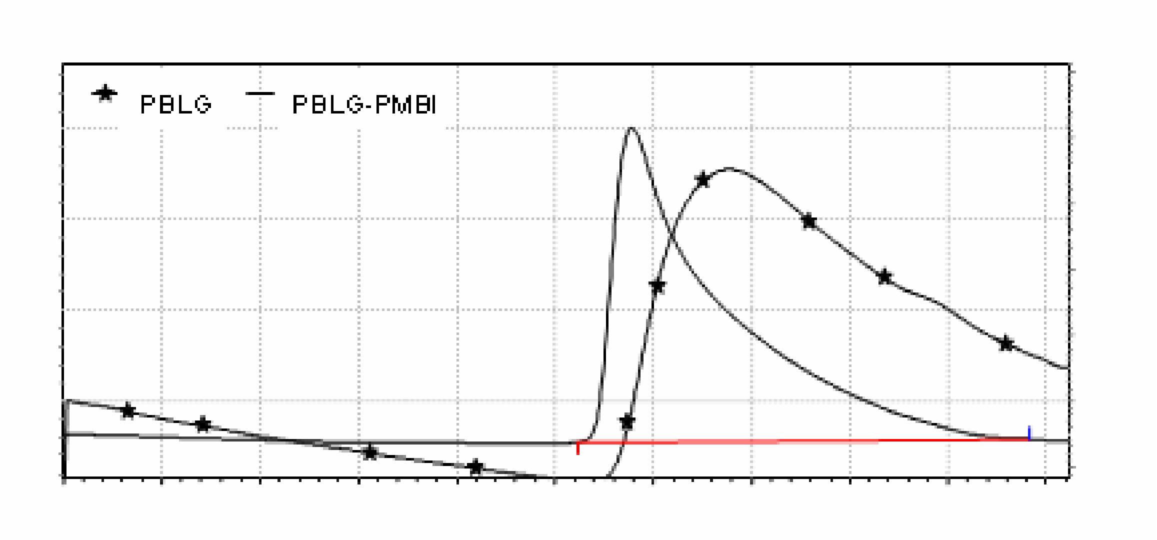

Figure S1. GPC-traces of poly(benzyl-L-glutamate) and poly(benzyl-L-glutamate)-*b*-poly((S)-(-)-α-methylbenzyl isocyanide) (PBLG-PMBI) in THF at 30 °C.

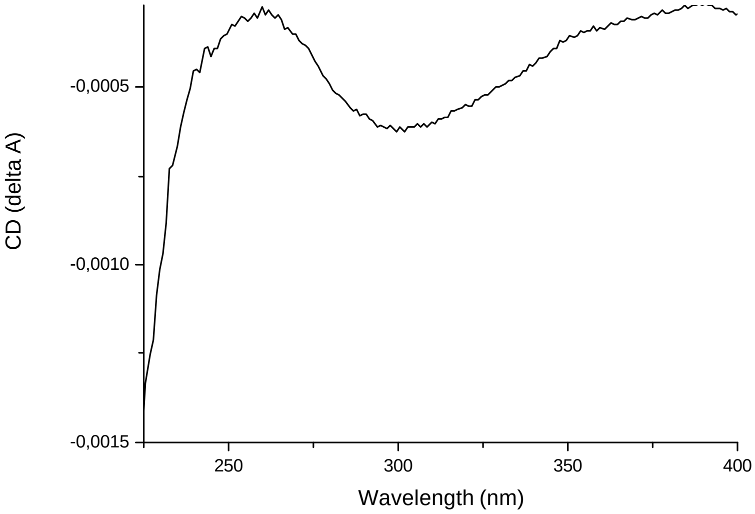

Figure S2. CD spectrum of PBLG-PMBI in chloroform (1 mg/ml) at 25 °C

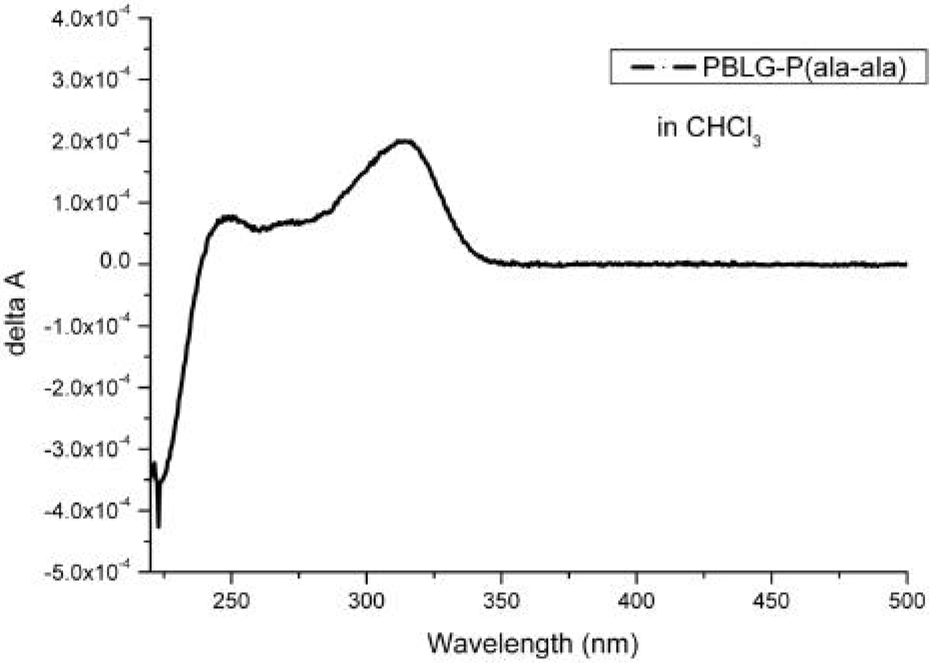

Figure S3. CD spectrum of PBLG-b-L,L-PIAA in chloroform at 25 °C.

References

[1] D.S. Poché, M.J. Moore, J.L. Bowles, *Synthetic Communications* **1999**, *29*, 843-854.
[2] J.J.L.M. Cornelissen, PhD thesis, Radboud University, The Netherlands, **2001**, 27-48.
[3] T.J. Deming *Macromolecules* **1999**, *32*, 4500-4502.