

## Supporting information

### Well-Defined (Co)polypeptides Bearing Pendant Alkyne Groups

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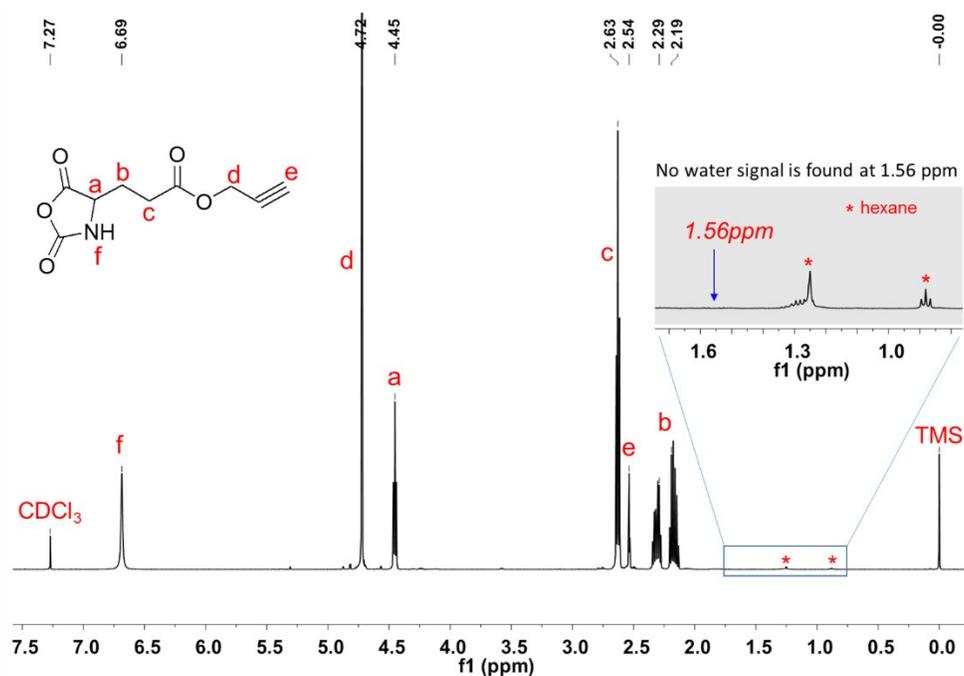
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#### Experimental Section

**General Methods.** All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under an argon atmosphere in a MBraun glovebox. Solvents were purified by using a MBraun SPS system. Anhydrous dichloromethane (DCM) was further dried by passing through an activated alumina column. Anhydrous DCM-*d*<sub>2</sub> was dried over P<sub>2</sub>O<sub>5</sub> at room temperature under argon overnight followed by distillation under reduced pressure. All other liquids were dried over activated 4 Å molecular sieves for a week and distilled before use, and solid materials were used as received. L-glutamic acid, propargyl alcohol, trimethylsilyl chloride and H-Glu(OBn)-OH was purchased from Sigma-Aldrich. Benzyl-Glu-NCA and Propargyl-Glu-NCA was prepared and purified according to published procedures.<sup>1</sup> *N, N'*-bis[3,5-bis(trifluoromethyl)phenyl] thiourea (abbreviated as TU-S) was synthesized and purified following literatures with modifications.<sup>2</sup>

**Instruments and Measurements.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV600 (FT, 600 MHz for <sup>1</sup>H; 150 MHz for <sup>13</sup>C) spectrometer. NMR assignments were confirmed by <sup>1</sup>H-<sup>1</sup>H (COSY), <sup>1</sup>H-<sup>13</sup>C (HMQC), and <sup>13</sup>C NMR (DEPT) experiments when necessary. *In situ* IR study of NCA polymerization was carried out by using ReactIR 45m with MCT Detector from METTLER TOLEDO. AutoChem. DiComp (Diamond) probe was connected via AgX 9.5mm x 1.5m Fiber (Silver Halide). Sampling is from 2800cm<sup>-1</sup> to 650cm<sup>-1</sup> at 8 wavenumber resolution and the automatic sampling interval is 10 seconds. The real-time concentration of NCA was quantified by measuring the intensity of NCA's anhydride peak at 1792 cm<sup>-1</sup> by FT-IR. The conversion of NCA was determined by comparing the NCA concentration during polymerization with the NCA concentration at *t* = 0. Polymer characterizations were carried out by combining an Agilent 1260 infinity SEC instrument with a multiangle laser light scattering (MALLS) apparatus at 60 °C. The system equipped with three Styragel<sup>®</sup> columns, a 1200 HPLC pump, an Optilab T-rEX RI detector, a ViscoStar-II viscometer and a DAWN HELEOS-II multiangle laser-light scattering (MALLS) detector at a laser wavelength of 690 nm (from Wyatt Technology). One guard column and three 7.8×300 mm columns (Styragel<sup>®</sup> HT 2 DMF, Styragel<sup>®</sup> HT 3 DMF and Styragel<sup>®</sup> HT 4 DMF) were used for polymer fractionation. HPLC-grade DMF (containing 0.1 M LiBr) was used as the mobile phase at a flow rate of 1.0 mL/min. The whole system, including columns and detectors, was maintained at 60 °C. Polymer solutions with concentrations between 5.0 and 10.0 mg/mL were injected at an injection volume of 200 μL. ASTRA software from Wyatt Technology was used to collect and analyze the data from the detectors.

**Polymerization procedure.** A typical procedure for the ring opening polymerization of NCA was performed in a 25 mL flask in a Braun Labmaster glovebox. To a vigorously stirred solution of initiator (**DMEA, MDEA, TEA or THEED**) and **TU-S** in 4 mL of solvent, a solution of 0.4g NCA monomer in 4 mL of solvent was added. AutoChem. DiComp (Diamond) probe of ReactIR 45m (METTLER TOLEDO) was connected to the reaction flask via a AgX 9.5mm x 1.5m Fiber (Silver Halide) to monitor the conversion of monomer. After specific time intervals, 0.2ml of the reaction mixture was taken out from the system and diluted to 10 mg /mL using DMF (containing 0.1 M LiBr). The solution was then analyzed by SEC to determine the molecular weight and dispersity of the obtained polypeptides. The remaining reaction mixture was poured into 10 mL methanol, sonicated and centrifuged to remove the solvent. The precipitated polymer was further dispersed in 10 mL fresh methanol, sonicated for 5 mins and removed methanol via centrifugation. The final polymer was collected and dried under vacuum overnight.



**Figure S1.**  $^1\text{H}$  NMR spectrum of propargyl-Glu-NCA (500MHz, anhydrous  $\text{CDCl}_3$ , 298K).

## Reference

1. (a) H. Lu and J. Cheng, *J. Am. Chem. Soc.*, 2007, 129, 14114. (b) A. C. Engler, H Lee and P. T. Hammond, *Angew. Chem., Int. Ed.*, 2009, 48, 9334;
2. C. B. Tripathi and S. Mukherjee, *J. Org. Chem.*, 2012, 77, 1592.