

Supplementary Information

Poly(β -alanoid-*block*- β -alanine)s: Synthesis via Cobalt-Catalyzed Carbonylative Polymerization and Self-Assembly

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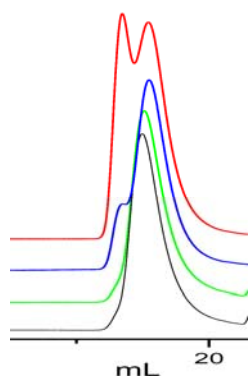


Figure S1. GPC chromatograms of homopolymer $(\beta\text{-MOBA})_{20}$ produced at room temperature at 1000 psi (—); 50 °C, 1000 psi (—); 80 °C, 1000 psi (—); and 50 °C, 150 psi (—).

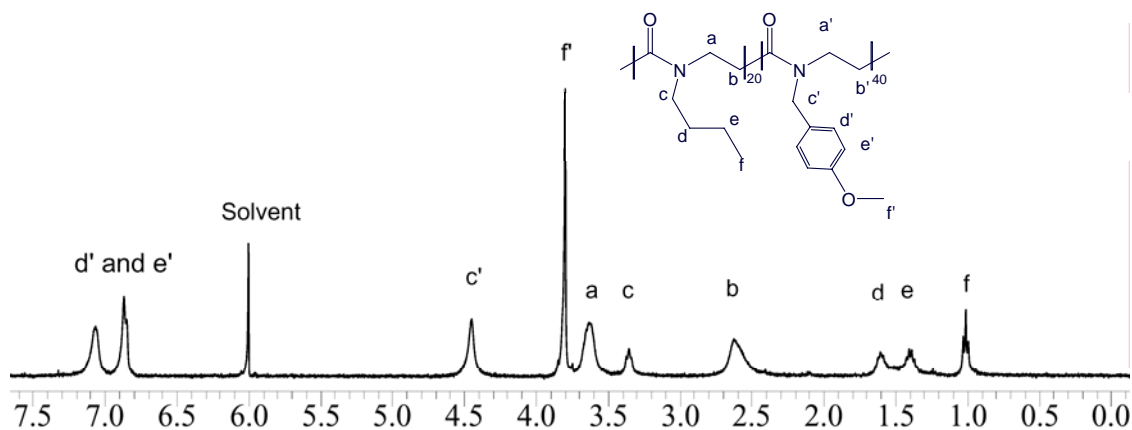


Figure S2. ^1H NMR spectrum of $(\beta\text{-}^n\text{BuA})_{20}\text{-}b\text{-}(\beta\text{-MOBA})_{40}$ diblock polymer in 1,1,2,2-tetrachloroethane- d_2 at 100 °C.

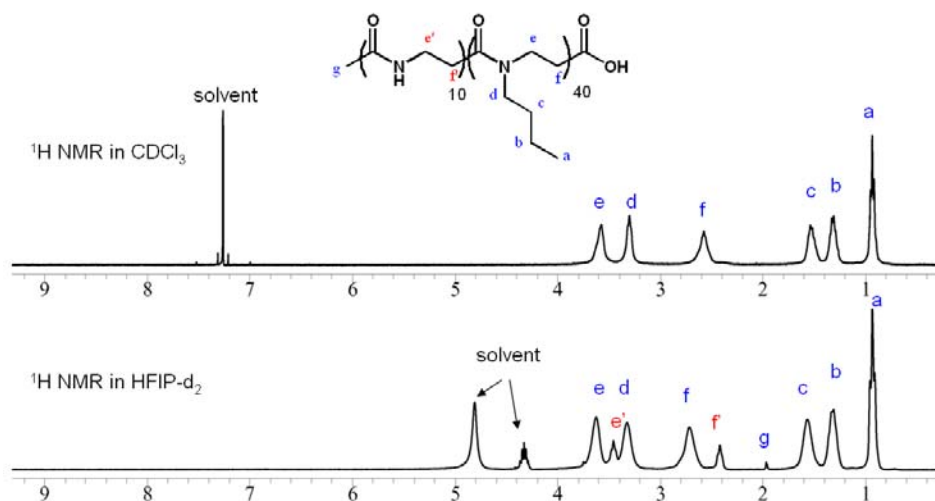


Figure S3. ^1H NMR spectra and assignments of **4** in CDCl_3 (top) and in HFIPA-d_2 (bottom). Chemical shifts are referenced against HFIPA peaks labelled with asterisks.

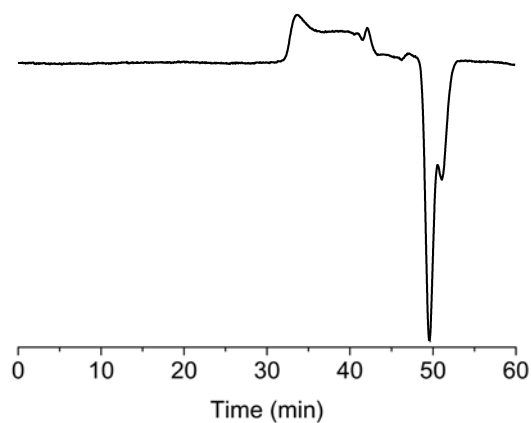


Figure S4. A representative GPC trace when chloroform was used as the eluent. Column temperature was at 45 °C. The particular sample is the poly(β Ala-*b*-ⁿBu β A) from entries 1 in Table 1.

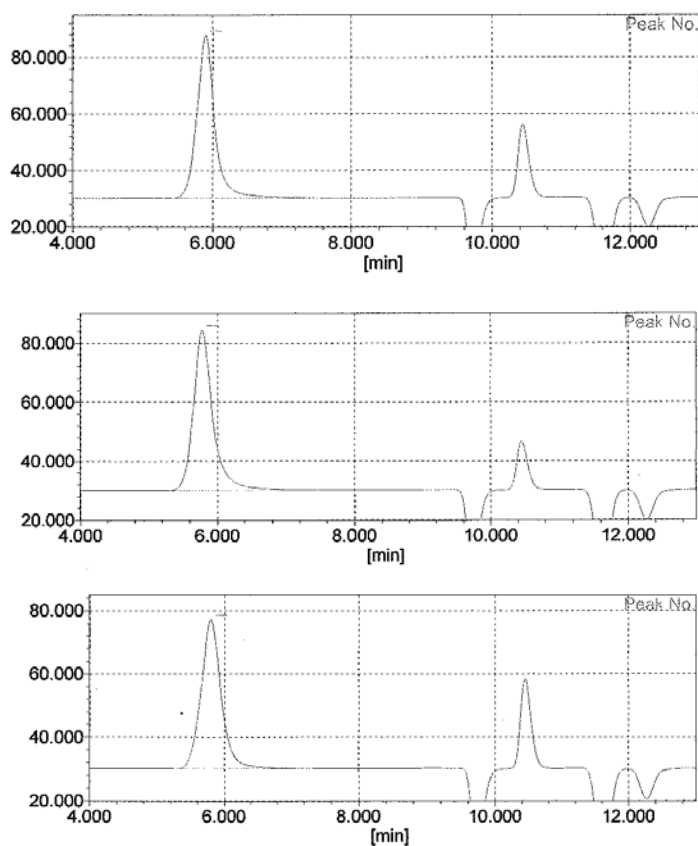


Figure S5. GPC traces of poly(β Ala-*b*-ⁿBu β A)s from entries 1, 2, and 4 in Table 1. HFIPA was the eluent. Column temperature was at 40 °C.

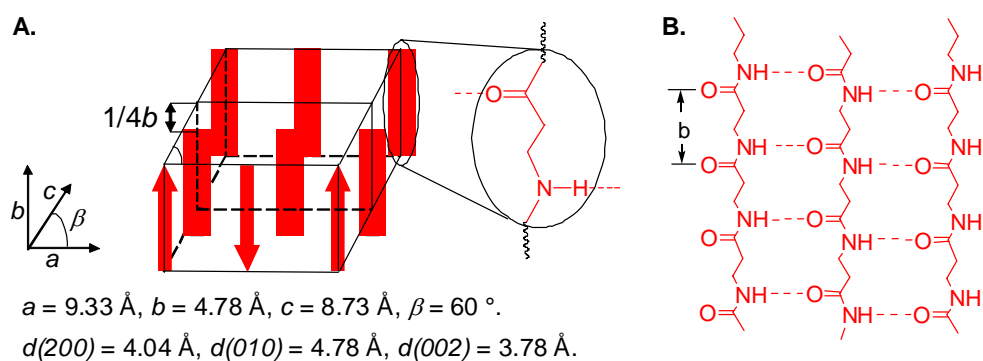


Figure S6. Solid state structure of poly(β -alanine) according to ref 3. **A.** Monoclinic unit cell of stacked antiparallel sheets with unit cell dimensions and d spacings at room temperature. The adjacent (002) planes are stacked with a displacement of $1/4$ of the identity period along the b axis. **B.** Sketch of the structure of the flat sheet approximately in the (002) planes.

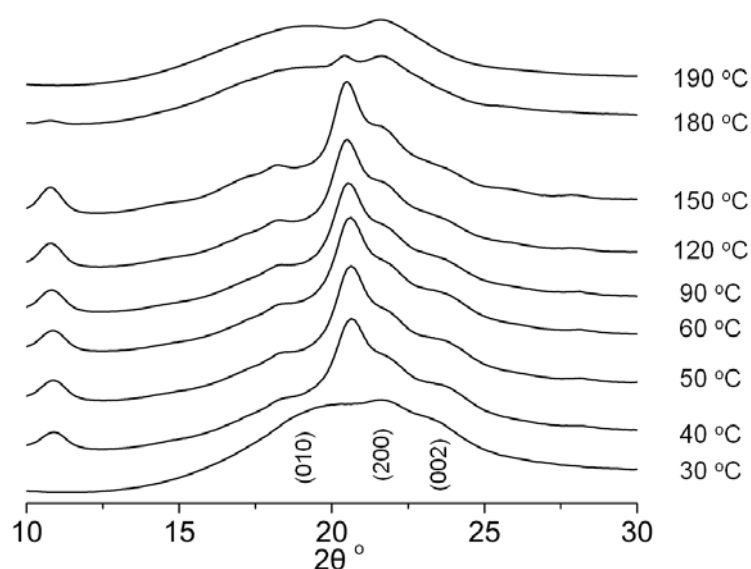


Figure S7. XRD of poly(β -alanine)₁₀-*b*-poly(^tBu β A)₄₀ at various temperatures.

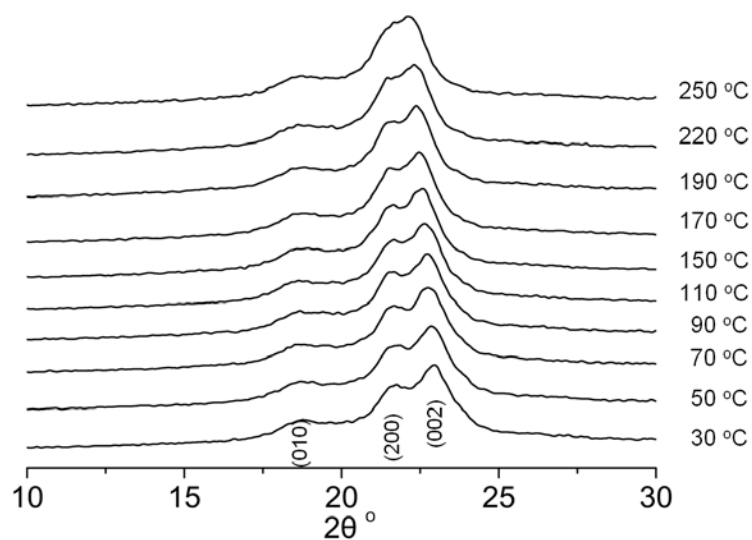


Figure S8. XRD of poly(β -alanine)₁₀ at various temperatures. Note that the (200) and (002) Bragg peaks gradually merge together as the temperature is raised.

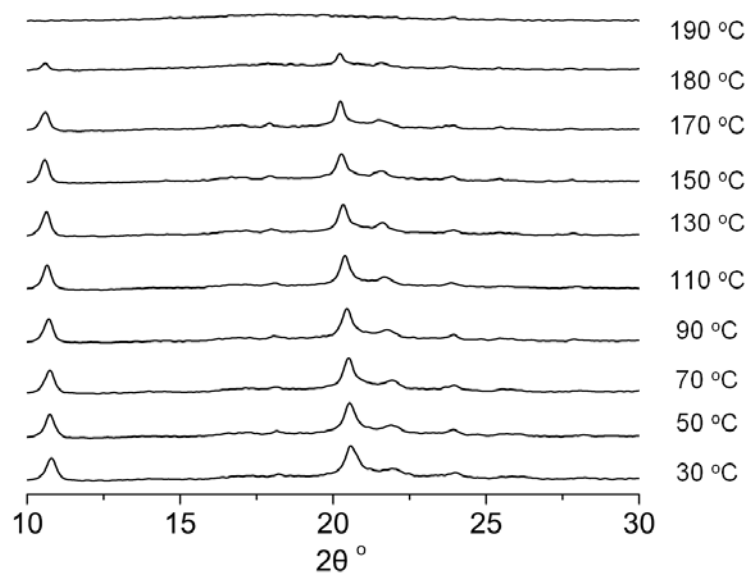


Figure S9. XRD of poly(ⁿBu β A) at various temperature.

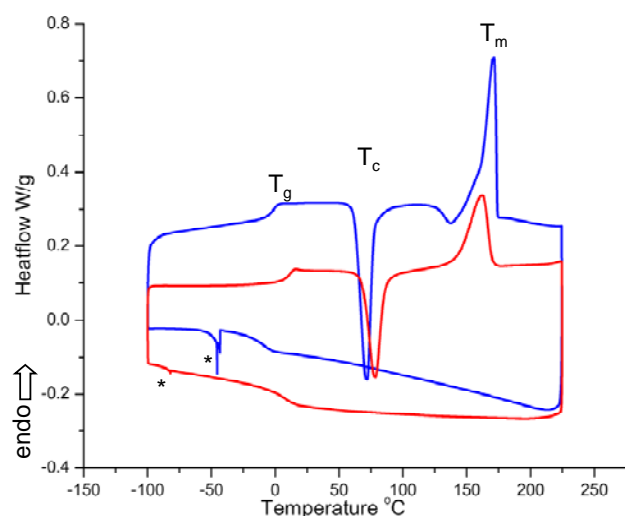


Figure S10. DSC traces of poly(ⁿBuβA) ($X_n = 40$) (blue) and **4** (red). Poly(βAla) has no thermal transitions before it composes at ~ 250 °C. The traces are the 2nd heating cycle at a scan rate of 5 °/min. The spikes on the cooling ramp labeled with asterisks are instrument noise observable with blank samples.

Static and dynamic laser light scattering. Laser light scattering (LLS) experiments were carried on a Brookhaven laser light scattering instrument equipped with BI-200SM Goniometer and PCI BI-9000AT correlator. A Melles Griot 35 mW He-Ne laser was used as light source (632.8 nm). A cylindrical glass scattering cell with diameter of 12 mm was placed in the center of thermostated bath with decahydronaphthalene used for refractive index matching. The BI temperature controller can adjust temperature from 10 to 80 °C (with an accuracy of temperature control of ± 0.01 °C). The glass scattering cells were extensively cleaned by ultrasonicing in THF and ethanol to eliminate any dust and impurity. Solutions were filtered into the scattering cells through 2.7 μm pore size filters.

For dynamic LLS experiments, in principle, the cumulant analysis of the measured intensity-intensity time-correlation function of the distributed object can lead to an accurate average line width $\langle \Gamma \rangle$. For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by

$$D = (\Gamma / q^2)_{q \rightarrow 0} \quad (1a)$$

or the hydrodynamic radius R_h via a relation of

$$R_h = k_B T / (6\pi\eta D) \quad (1b)$$

where q is the scattering wave vector, k_B , Boltzmann constant, η , the solution viscosity and T , the absolute temperature. The hydrodynamic diameter D_h can be deduced by $D_h = 2R_h$.

In static LLS experiments, from the excess time-averaged scattering light intensity $I_{ex} = I_s(\text{solution}) - I_s(\text{solvent})$, the excess Rayleigh Ratio R_{ex} can be deduced

$$R_{ex} = I_{ex} R^2 / I_{INC} \quad (2)$$

where R and I_{INC} are the Rayleigh ratio and incident laser intensity, respectively. In dilute solution regime, the classical Zimm equation holds

$$\frac{KC}{R_{ex}} \cong \frac{1}{MP(q)} + 2A_2C \quad (3a)$$

where K , C , M , $P(q)$ and A_2 are the optical constant, the polymer concentration, the particle molar mass, the particle scattering factor (also know as the form factor) and the second virial coefficient, respectively. For mono-disperse small particles when $qR_g \ll 1$,

$$P(q) = 1 - q^2 R_g^2 / 3 \quad (3b)$$

where R_g is the radius gyration of the scattering objects. For low concentration and when $qR_g \ll 1$, we will have

$$\frac{KC}{R_{ex}} \cong \frac{1}{M} + \frac{q^2 R_g^2}{3M} \quad (3c)$$

Figure S11 is the hydrodynamic diameter distribution $f(D_h)$ of the micelles in chloroform solution at different concentration for sample $\beta\text{Ala}_{10}\text{-}b\text{-}^n\text{Bu}\beta\text{A}_{40}$. The block copolymer self-assemblies have hydrodynamic diameter ranging from a few tens nanometers to several hundred nanometers. The averaged hydrodynamic diameter of micelle size for 1.0 mg/ml is 127 nm, and 192 nm for 4.5 mg/ml solution.

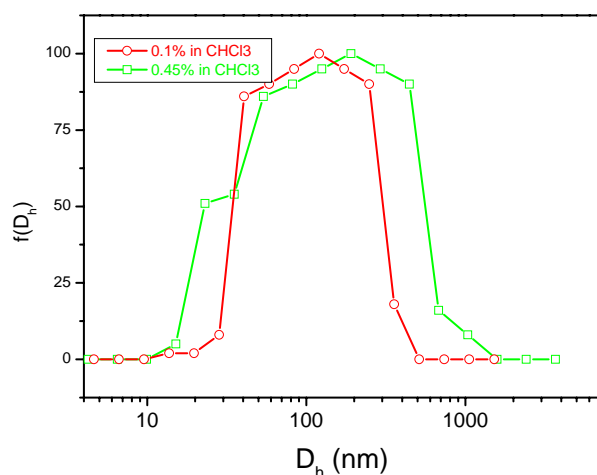


Figure S11. Hydrodynamic diameter distribution $f(D_h)$ of the micelles of $\beta\text{Ala}_{10}\text{-}b\text{-}^n\text{Bu}\beta\text{A}_{40}$ in chloroform solution at different concentration: (—) 1.0 mg/ml and (—) 4.5 mg/ml.

Figure S12 is the static laser light scattering of $\beta\text{Ala}_{10}\text{-}b\text{-}^n\text{Bu}\beta\text{A}_{40}$ at 1.0 mg/ml in chloroform. Assuming A_2C can be neglected since the concentration is low, we can obtain the apparent molecular weight of self-assembled particles, 2.0×10^8 g/mol by equation 3c. This indicated there is about 40,000 $\beta\text{Ala}_{10}\text{-}b\text{-}^n\text{Bu}\beta\text{A}_{40}$ chains assembled in one micelle on average. From the slope, we can estimate the apparent radius of gyration to be 239 nm. The ρ parameter, which is the ratio of R_g to R_h , is $239/(127/2) = 3.76$. The value suggests that the particles likely have large aspect ratios.

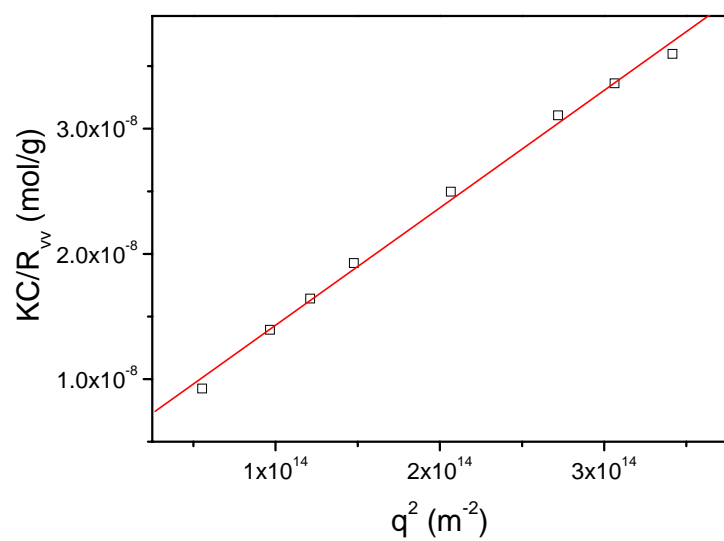


Figure S12. Static laser light scattering of β Ala₁₀-*b*-Bu β A₄₀ at 1.0 mg/ml in chloroform at different q value range.