Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

pH-Responsive and Selective Protein Adsorption on an Amino Acid-Based Zwitterionic Polymer Surface

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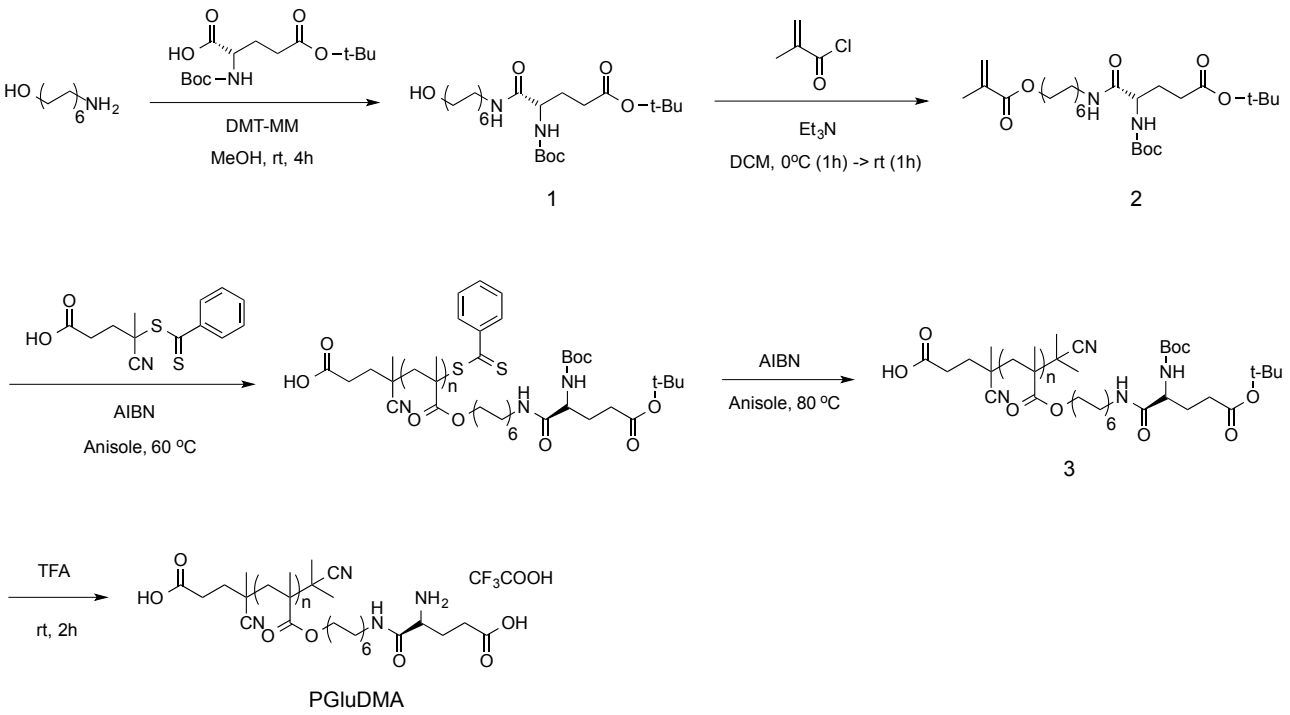
General Considerations

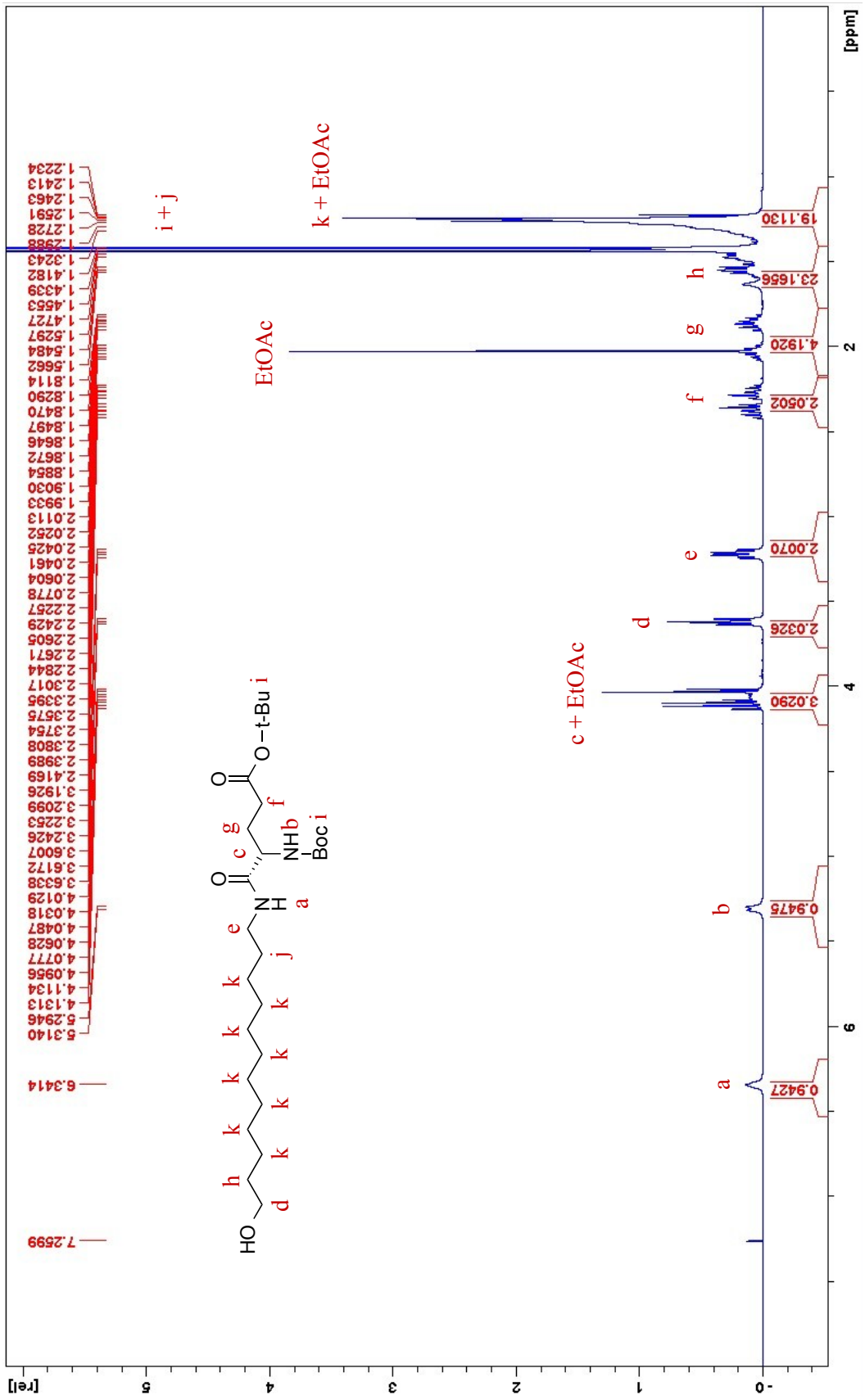
All reactions were carried out under argon atmosphere, and all of solvents were dehydration by standard methods. The progress of reactions was monitored with thin layer chromatography (TLC). The products were detected by using UV (254 nm) or staining with a basic solution of potassium permanganate. All products were purified by column chromatography with silica gel 60 (240 – 400 mesh). Nuclear magnetic resonance spectra were recorded with a 400 MHz BRUKER spectrometer using chloroform-*d* or methanol-d_4. Chemical shifts (δ) were expressed by parts per million from solvent resonance as the internal standard. A FAB-MS spectrum was recorded with 3-Nitrobenzyl alcohol as the matrix.

Synthesis Procedure

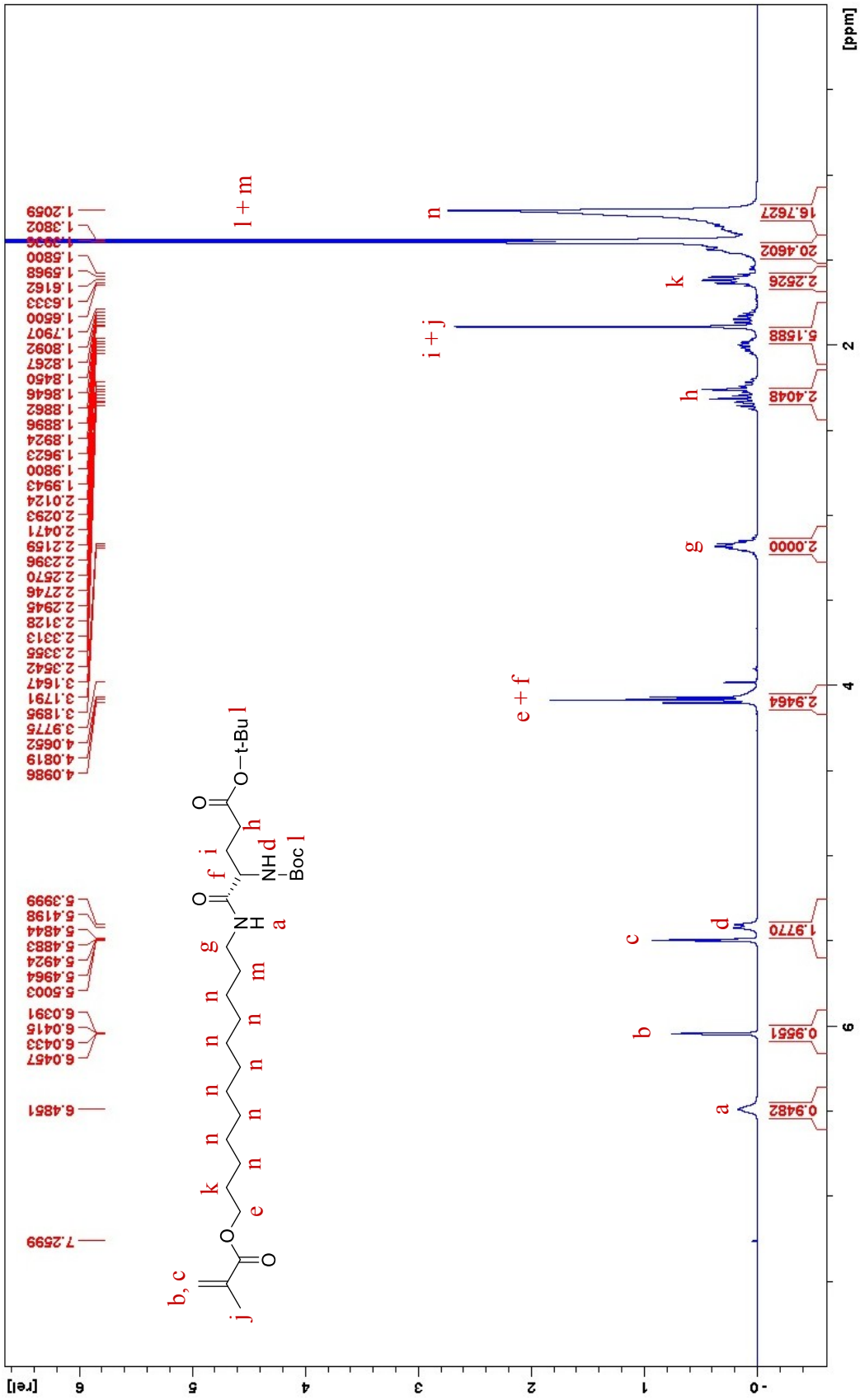


Scheme S1. Synthesis Scheme of PGluMA via RAFT Polymerization

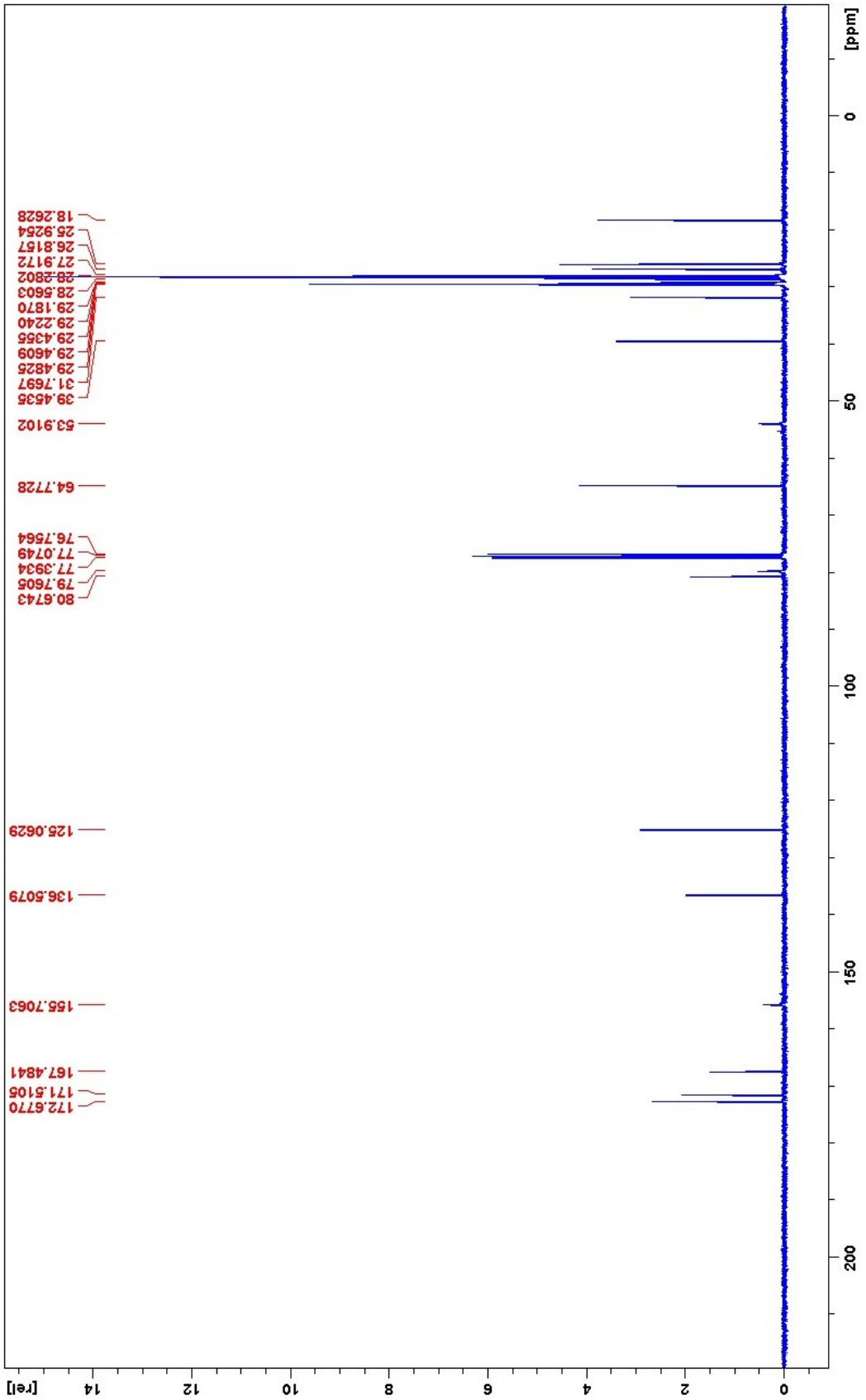
^{1}H-NMR Spectrum of **1**



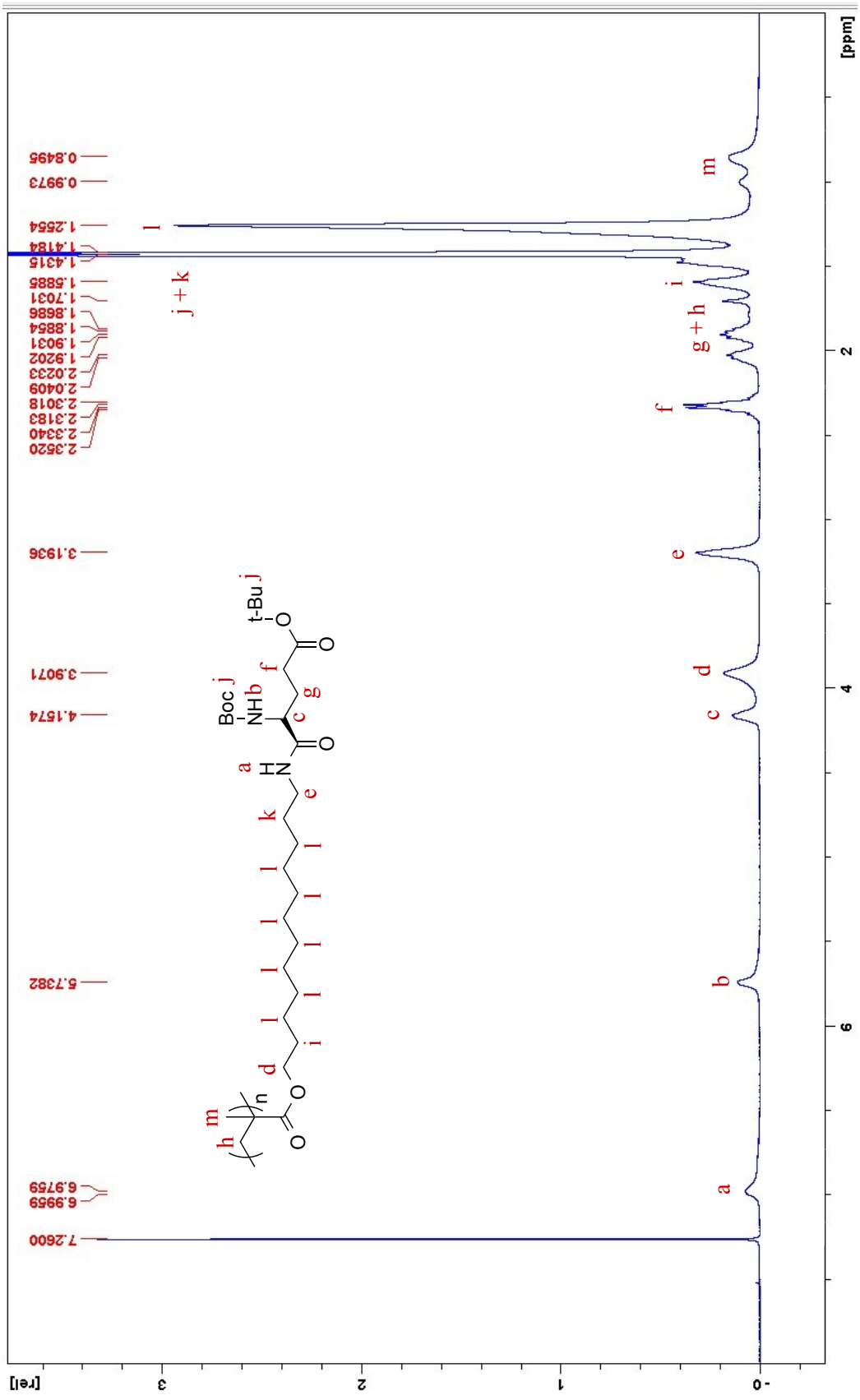
^{1}H-NMR Spectrum of **2**



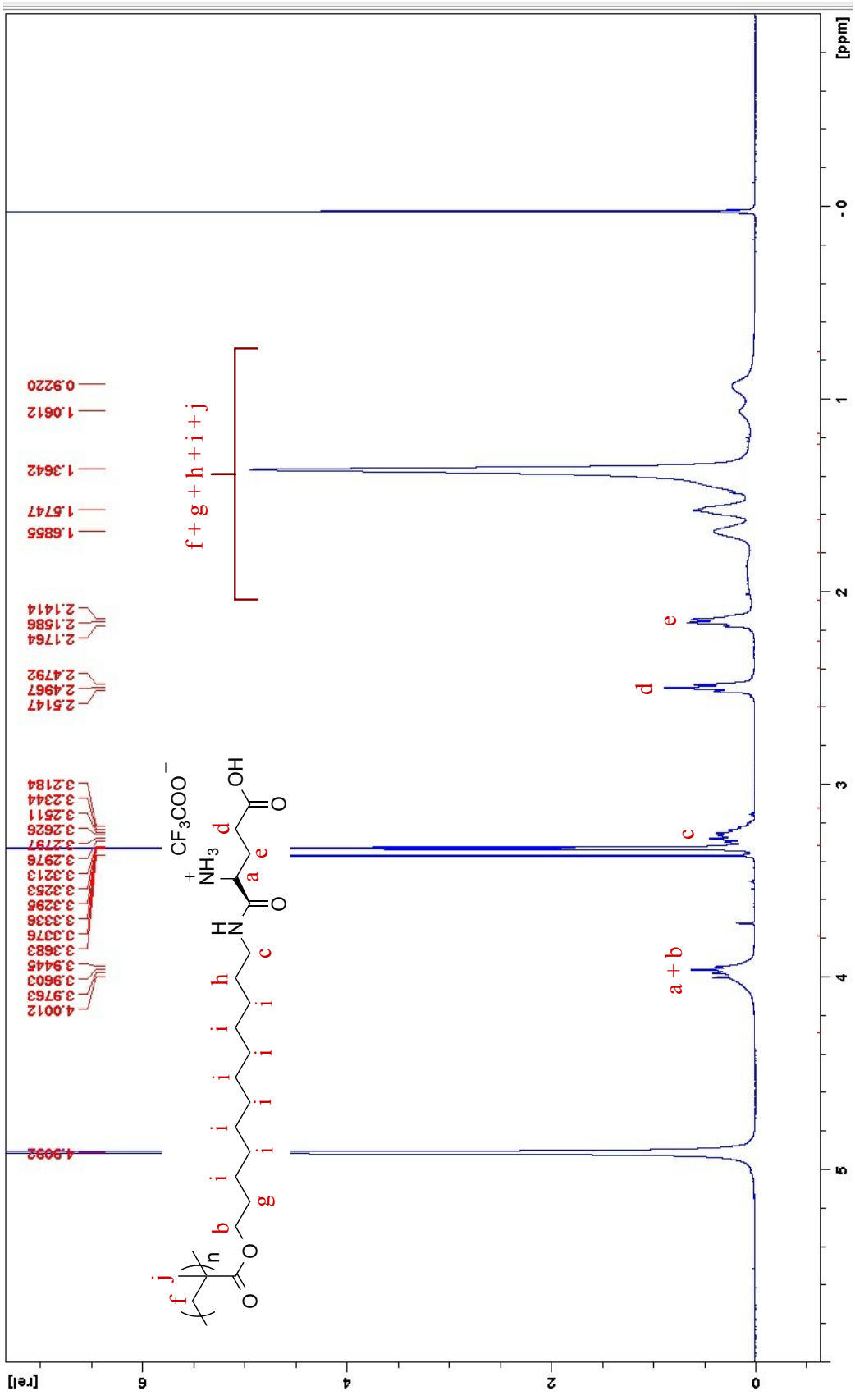
^{13}C-NMR Spectrum of **2**



^{1}H-NMR Spectrum of **3**



^{1}H-NMR Spectrum of **PGluDMA**



Characterization of a polymer

The weight average molecular weight of PGluDMA was calculated from the molecular weight of the precursor polymer (polymer 3). Figure S1 shows the concentraton dependence of refractive index increment and SEC-MALS fractogram of polymer 3 in THF. We calculated the weight average molecular weight and the molecular weight distribution of the polymer 3 to be 4.3 × 10^4 g/mol and 1.10, respectively. From the values, the molecular weight of the final product, PGluDMA, was determined to be 3.9 × 10^4 g/mol.

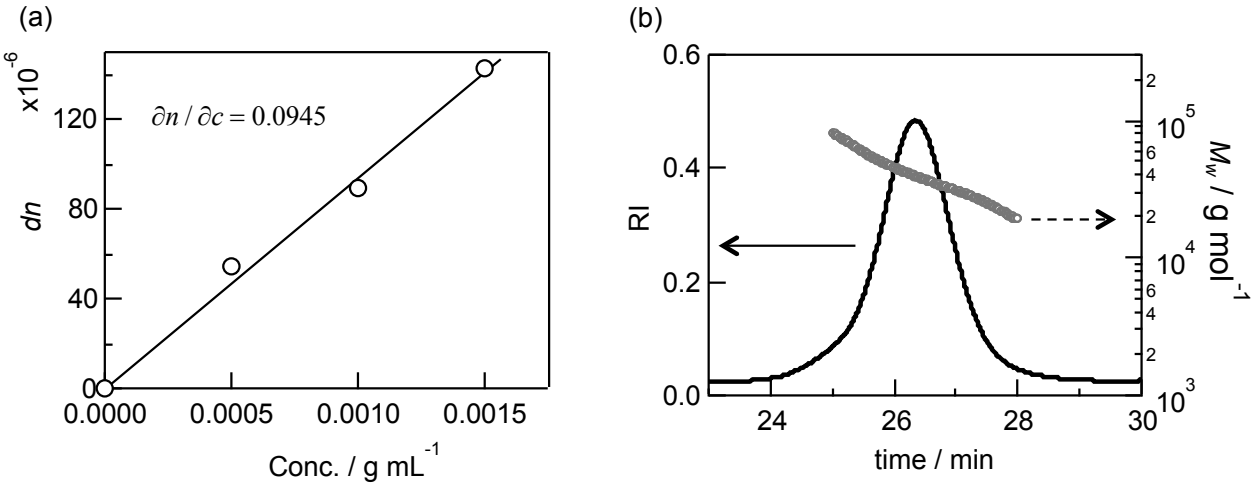


Figure S1. Concentraton dependence of refractive index increment (a) and SEC-MALS fractogram (b) of polymer 3 in THF.

Thermal property of PGluDMA was examined by deferential scanning calorimetry (DSC) with a SII DSC6220 (Seiko Instruments Inc., Japan) with the heating ratio of 10 ℃/min^{-1}. Figure S2 shows that the glass transition temperature (T_g) was determined to be 10 ℃. There were two transition peaks at 85 and 114 ℃. At the first peak temperature, the partially melted polymer with an optical texture was observed by polarized optical microscopy (POM), and then the polymer was completely melted with the optical texture above 100 ℃.

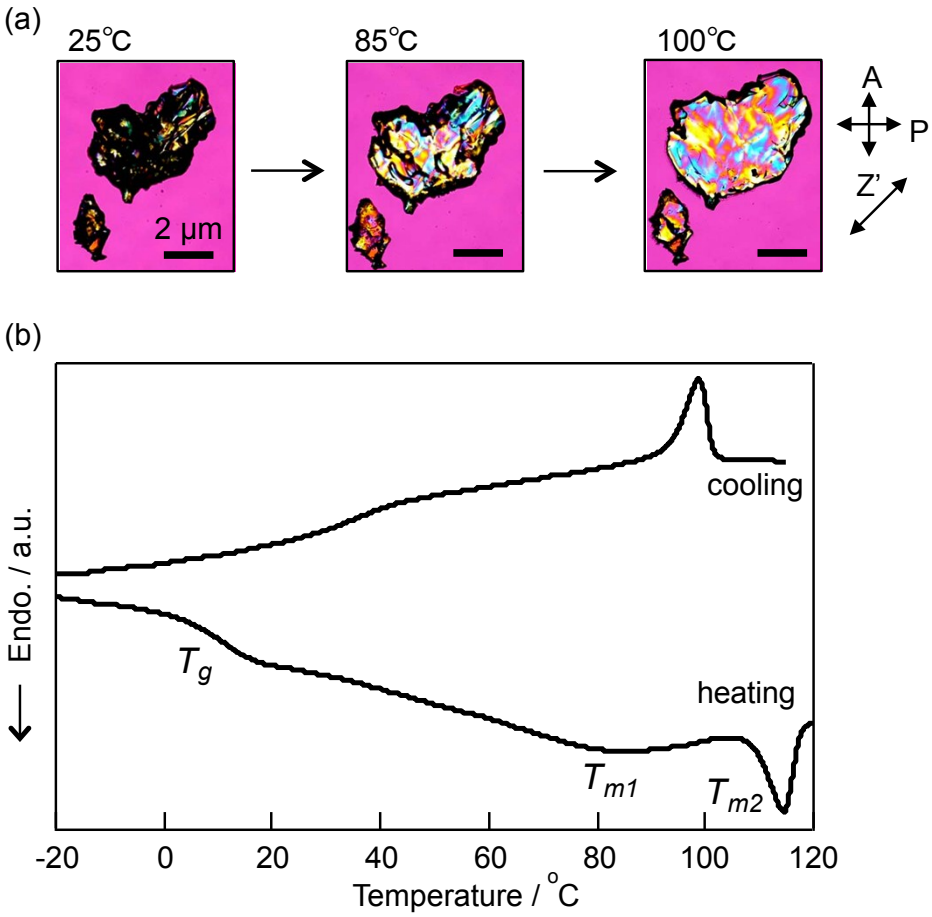


Figure S2. (a) POM photographs for PGluDMA powders at 25℃, 85℃, 100℃. (b) DSC thermogram for PGluDMA powders. Before the measurement, the powders were thermally

annealed at 100 ℃ for over 6 hours under *vacuo*.

We carried out small and wide angle X-ray scattering (SAXS and WAXS) measurements for PGluDMA. Figure S3 shows the scattering profiles for the bulk state of the polymer after annealing at 100℃ for over 6 hours under *vacuo*. The relative scattering vector was 1 : 2, indicating that lamellar structures were formed in the bulk. The lamellar thickness determined from the *q* value at first peak is 3.75 nm. The *d*-spacing determined from the peak in WAXS profile is 0.460 nm, corresponding to the interdistance between the alkyl chains in the polymer side chains.

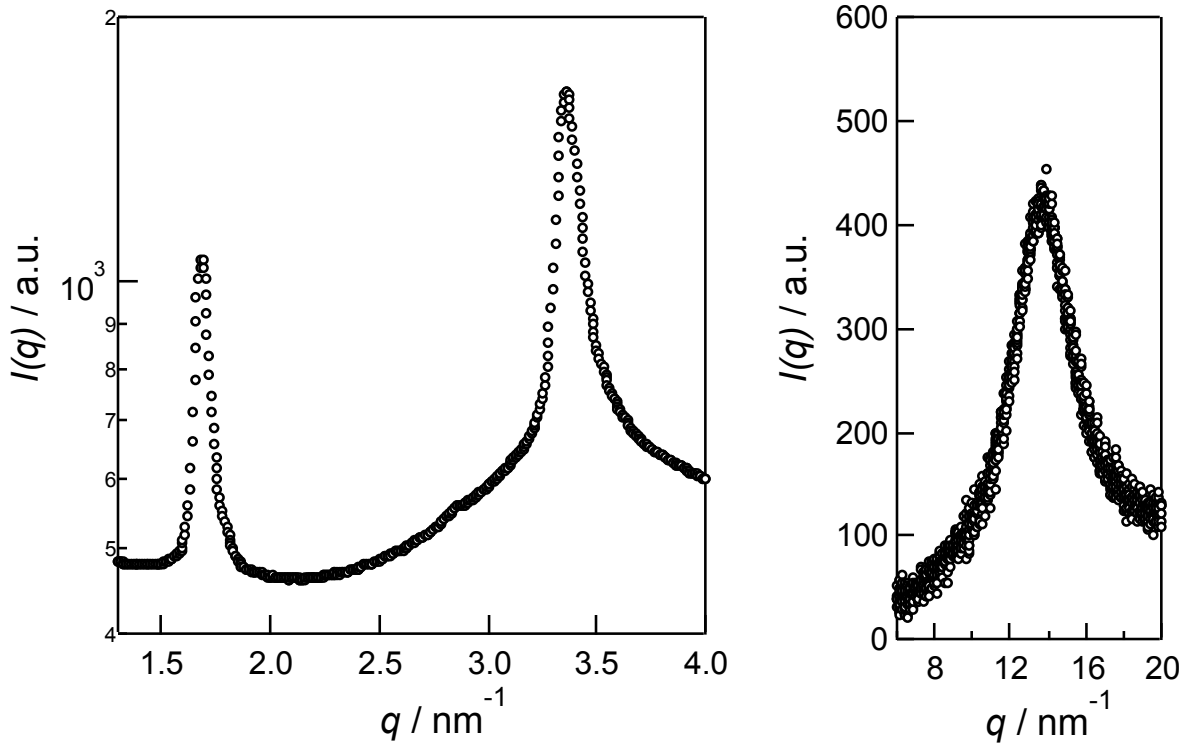


Figure S3. SAXS and WAXS profiles of the bulk state of PGluDMA after annealing at

100℃ for over 6 hours in *vacuo*.

Nanostructures in a polymer film

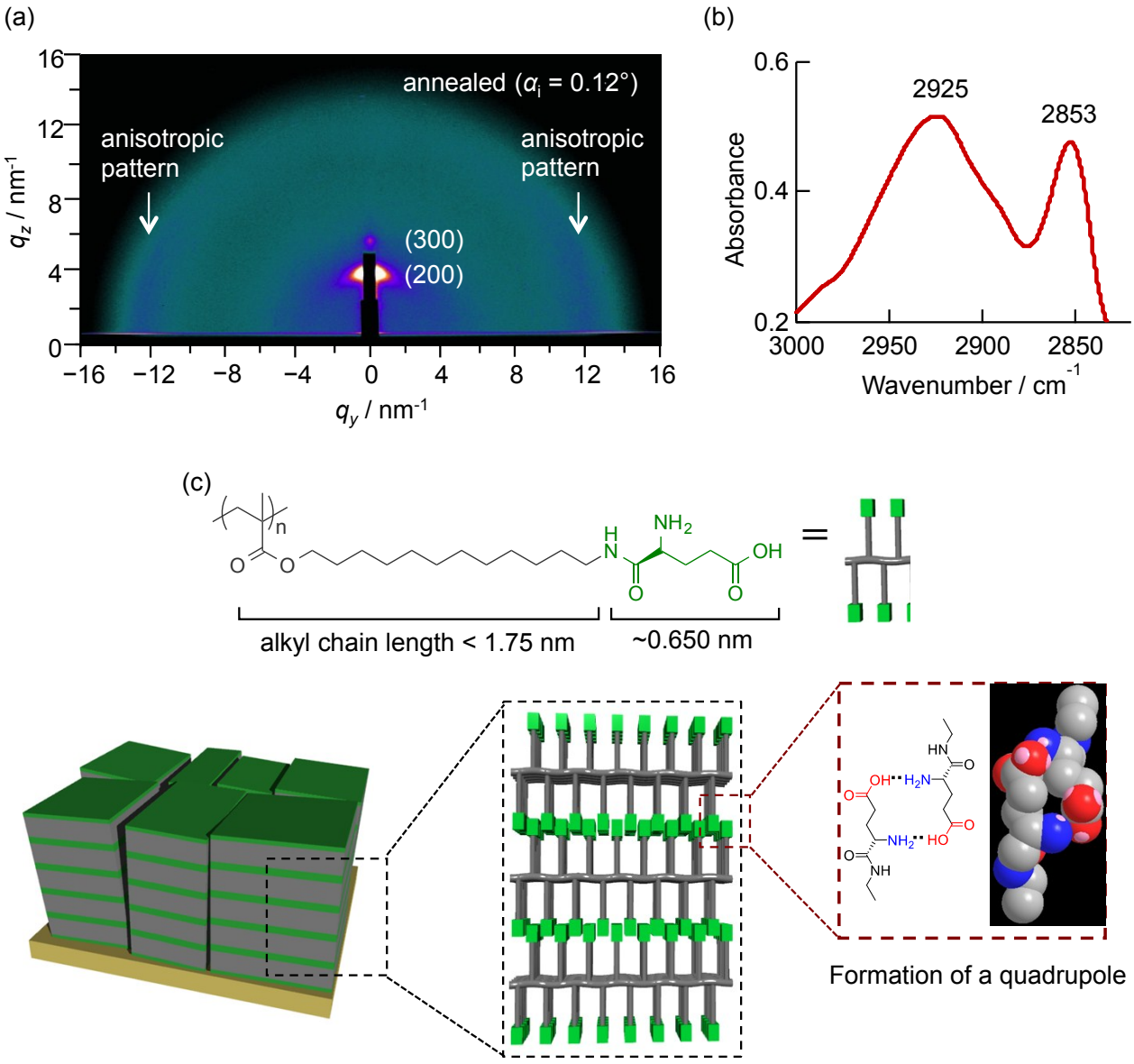


Figure S4. (a) Representative 2D GISAXS patterns for the thermally annealed PGluDMA film. (b) FT-IR spectrum for thermally annealed PGluDMA powders. The peaks at 2853 and 2825 cm^{-1} indicate the alkyl conformation in the polymer side chain includes gauche structures. [1–2] (c) Proposed nanostructural model of PGluDMA in the thin film. The

formation of a quadrupole through two primary amines and carboxylic acids in glutamic acid moieties was calculated with MOPAC.

Definition of static contact angle

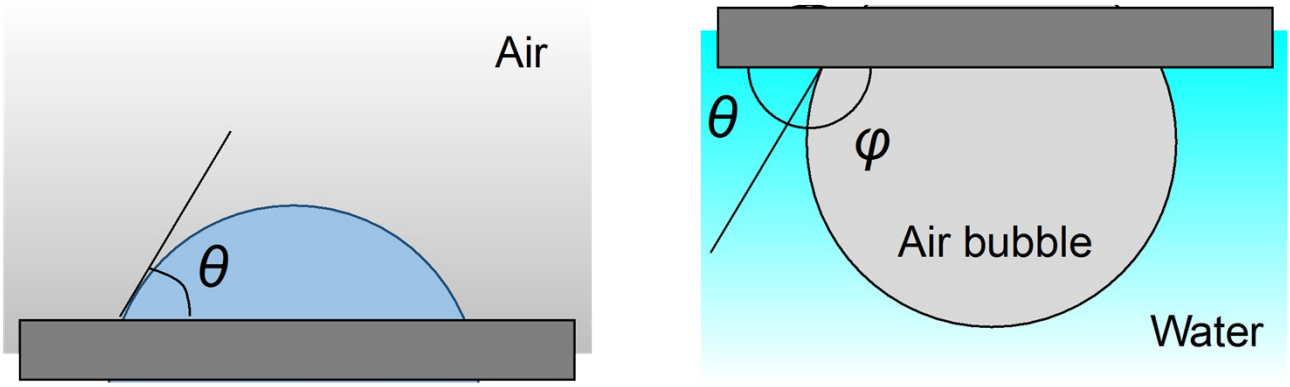


Figure S5. Definition of static contact angle: θ and φ.

Atomic Force Microscopy images

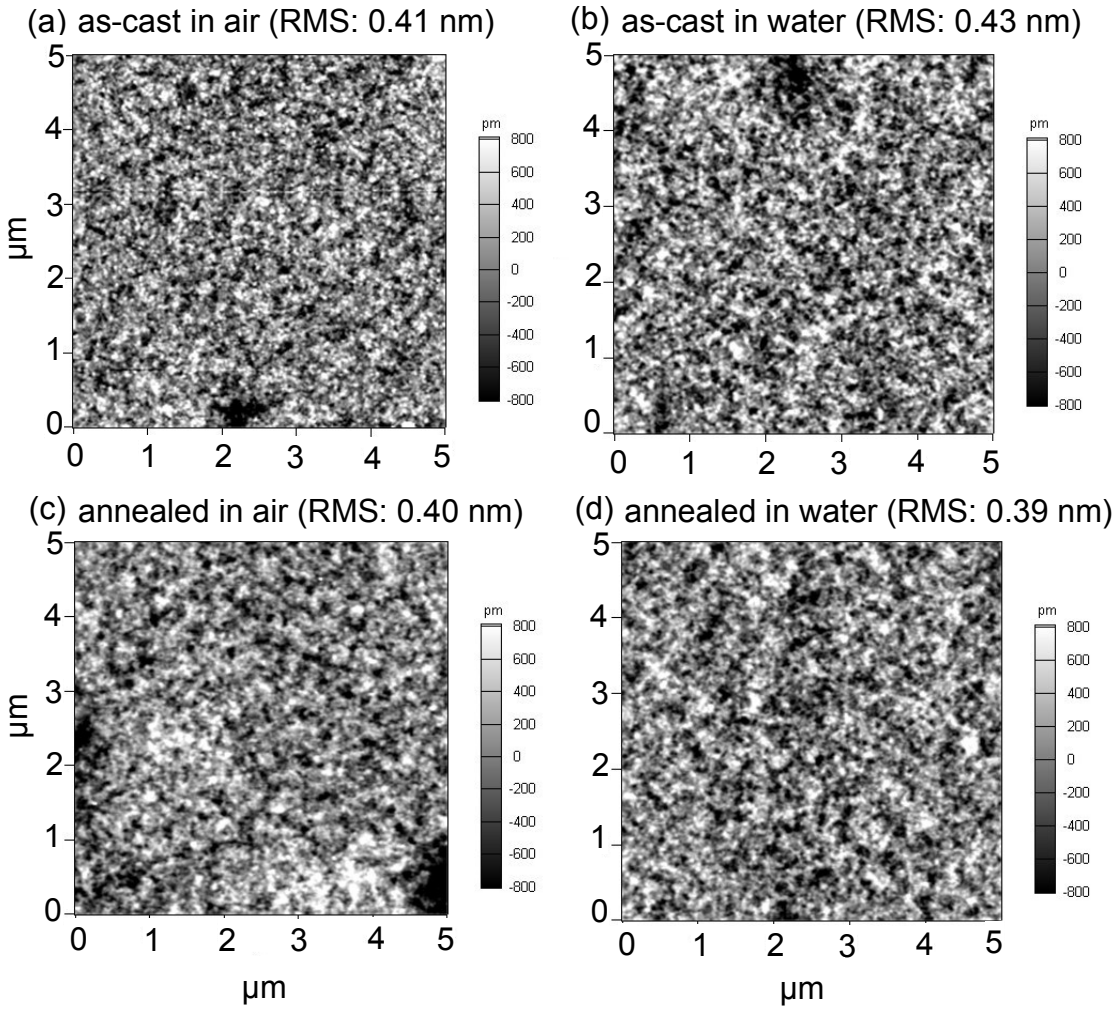


Figure S6. AFM images on the as-cast and the thermally annealed PGluDMA films in air (a, c) and in water (b,d).

Quartz Crystal Microbalance (QCM)

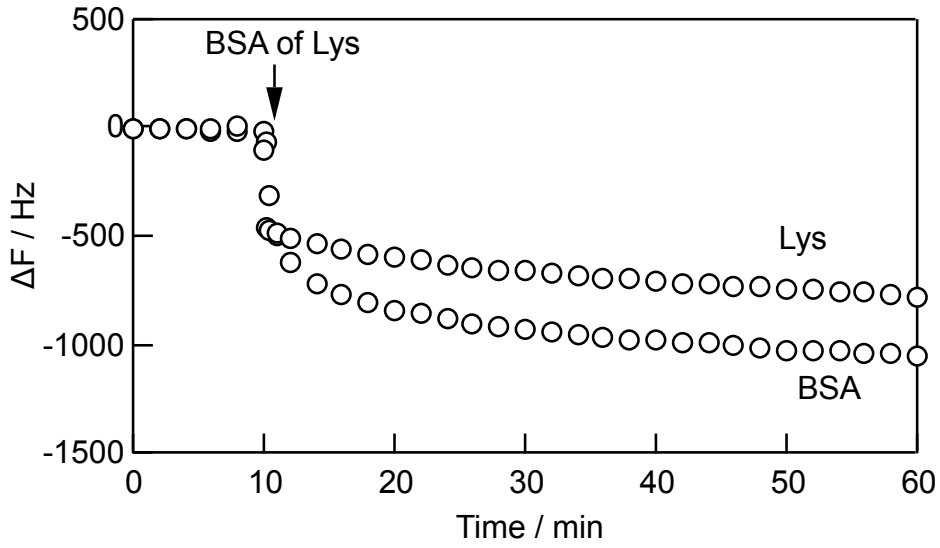


Figure S7. Frequency shifts for BSA and Lys adsorption onto gold in 100 mM Tris-HCl buffer solution (pH 7.5).

Electron Density Distribution of a Glutamic Acid Derivative

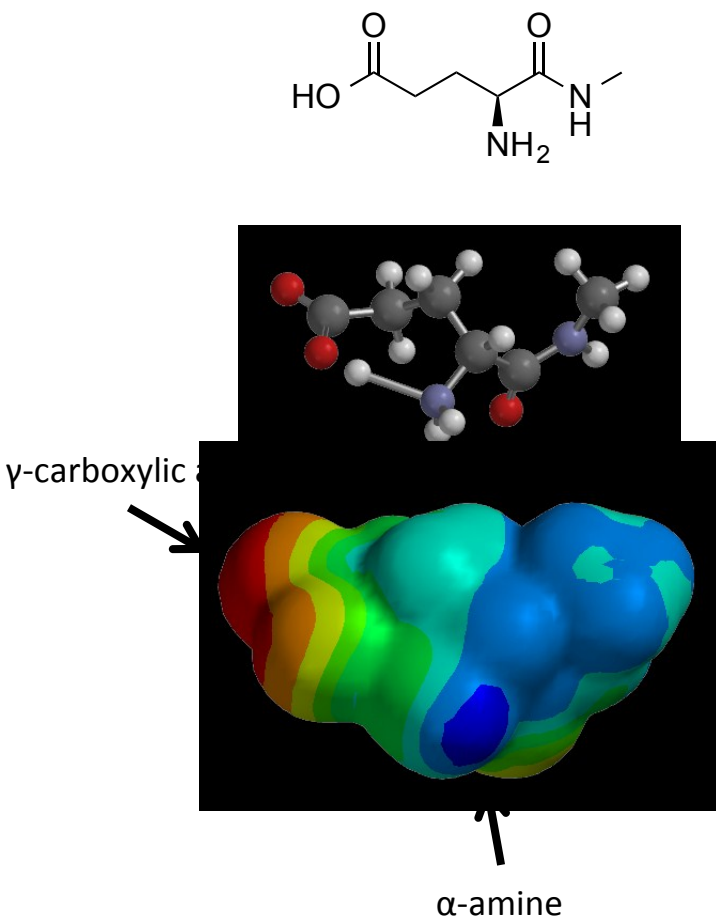


Figure S8. Energy-minimized structure and electron density distribution of glutamic acid. The calculation was carried out using ab initio Hartree-Fock method with 6-31G basis set.

References

[1] R. Mendelsohn, J. W. Brauner, A. Gericke, *Annual Review of Physical Chemistry* 1995, **46**, 305-334.

[2] C. Topacli, A. Topacli, B. Teşneli, T. Richardson, İ. Gürol, V. Ahsen, *Journal of Molecular Structure* 2005, **752**, 192-197.