Supporting Information

Modulating the Crystallinity, Mechanical Properties, and Degradability of Poly(ε-caprolactone) Derived Polyesters by Statistical and Alternating Copolymerization

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1. ^{1}H NMR spectroscopies of the three polymers

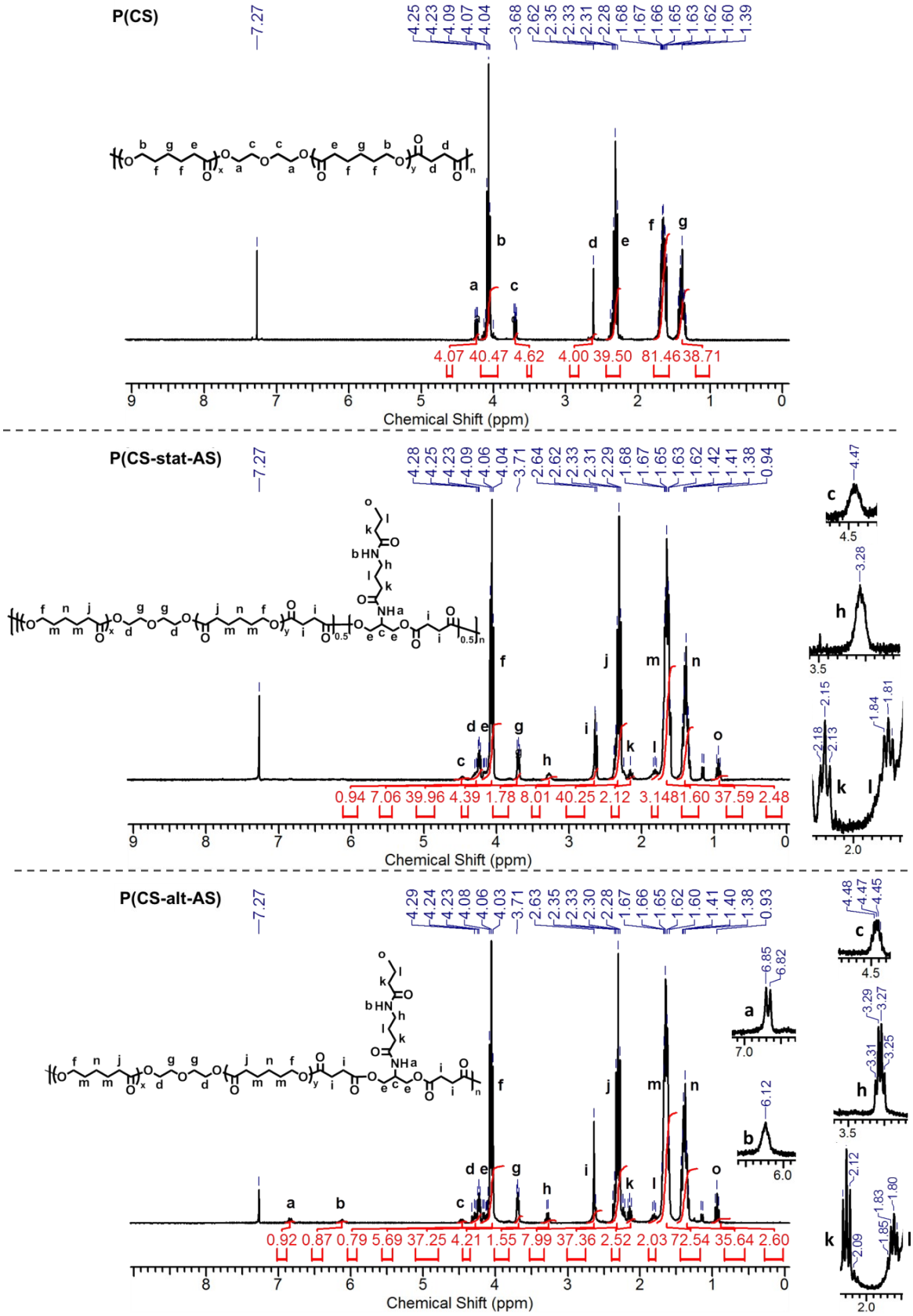


Figure S1. ^{1}H NMR spectroscopies of the three polymers.

2. Obtaining molecular weigth from SEC

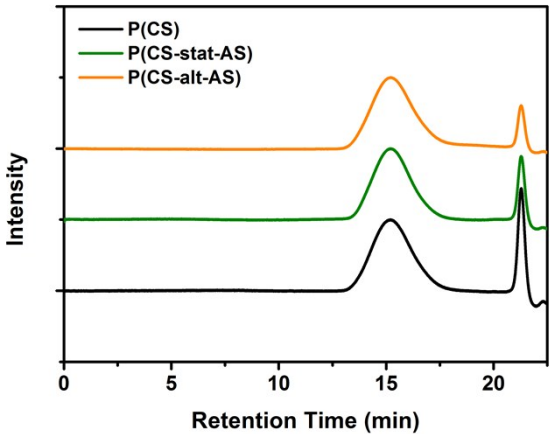


Figure S2. SEC curves of the three polymers in THF.

3. Obtaining T_m of three polyesters from DSC

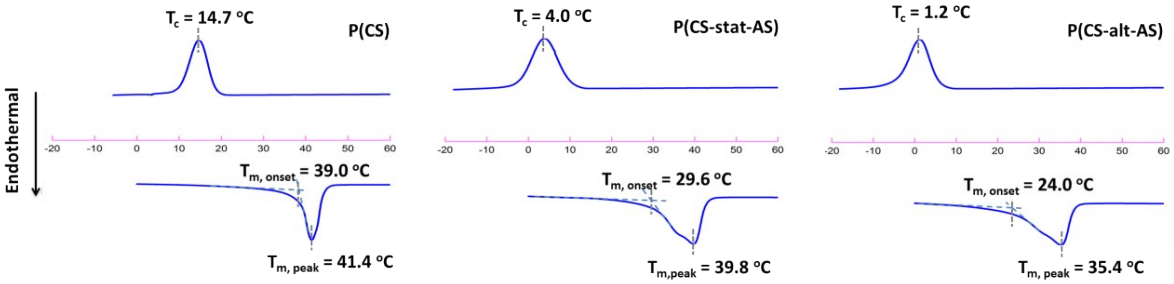


Figure S3. Determination of T_m of three polyesters from DSC

4. Obtaining T_g and T_m of the three polyesters from DMA

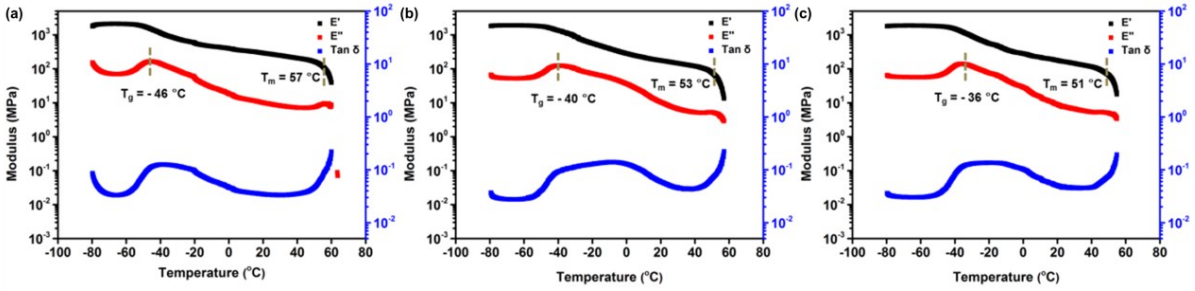


Figure S4. Determination of T_g and T_m of (a) P(CS), (b) P(CS-stat-AS) and (c) P(CS-alt-AS) from DMA.

5. Engineering stress-strain curves for the three polymers under various conditions

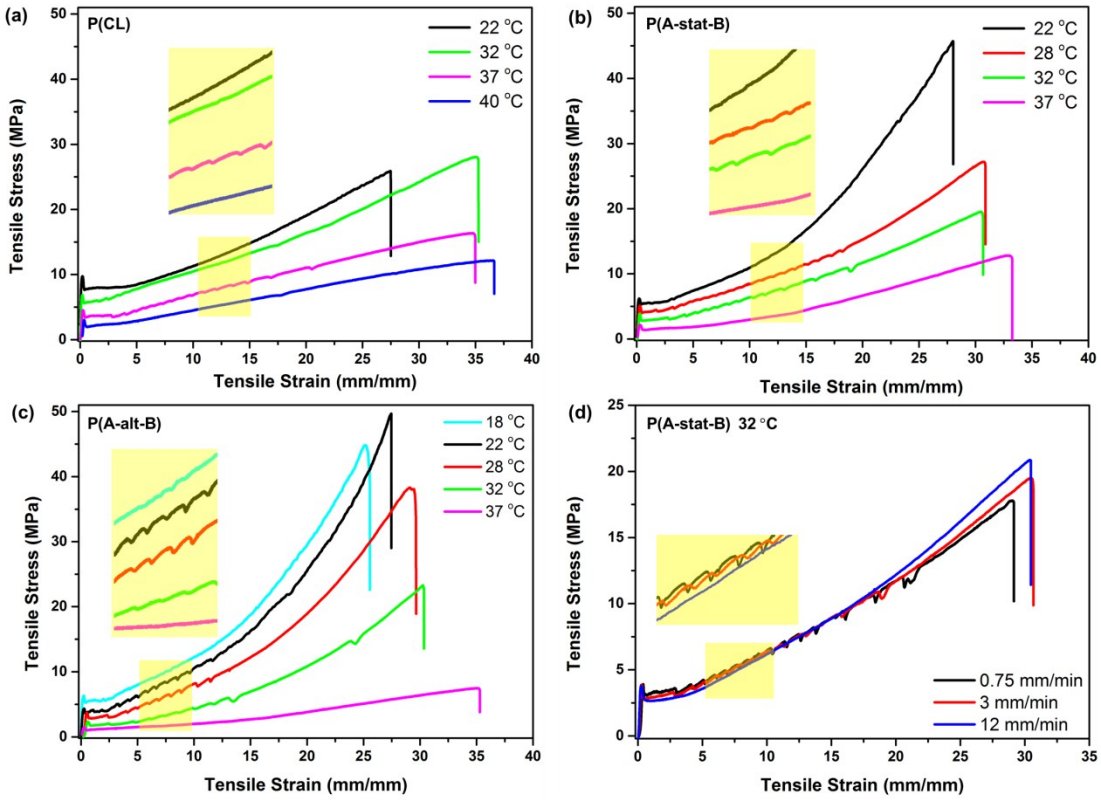


Figure S5. Tensile testing of (a) P(CS), (b) P(CS-stat-AS) and (c) P(CS-alt-AS) at various temperatures to study the dependence of sawtooth-like profiles on temperature; (d) tensile testing of P(CS-stat-AS) at 32 °C using different strain rates.

Stress-strain curves of the three polymers under different temperatures are shown in **Figure S5 (a)**, **(b)** and **(c)**. The speed of crosshead was set as 3 mm/min. The sawtooth showed up for specimens in the temperature range close to their T_m. In **Figure S5 (d)**, the tensile testing was performed at 32 °C, with different stetching rates of 0.75 mm/s, 3 mm/s ad 12 mm/s being used. The sawtooth-like profile only appeared with low stretching rates (0.75 mm/s and 3 mm/s).

6. Polymer specimens during and after tensile testing

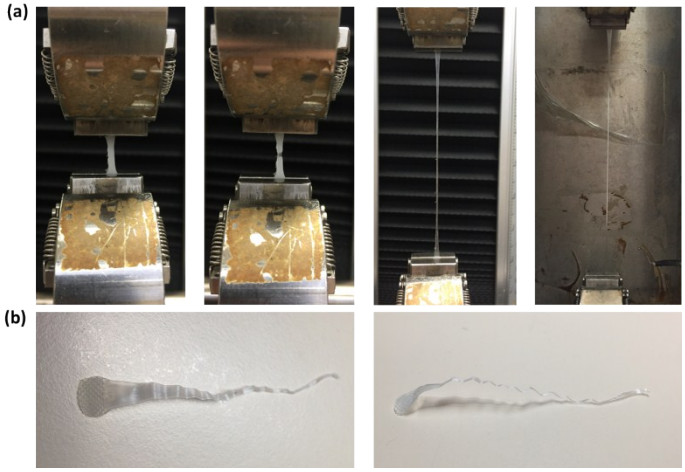


Figure S6. (a) Specimen during tensile testing, (b) Specimen in zigzag shape after fracture.

As an illustration, pictures of P(CS-alt-AS) during tensile testing at 22 °C are shown in **Figure S6**. Necking was observed on specimen after the initial linear region, indicating the plastic deformation. After fracture, the specimen was in zig-zag shape.

7. 1D WAXD figures for the three polyesters before and after tensile test

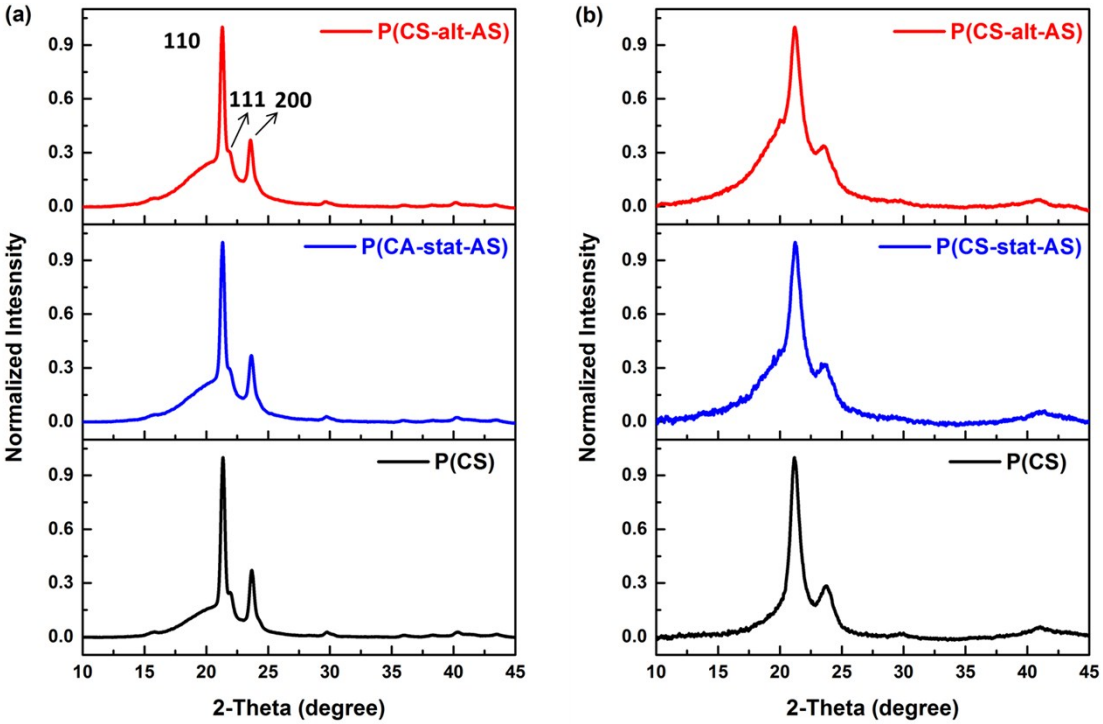


Figure S7. 1D WAXD figures of P(CS-alt-AS), P(CS-stat-AS), and P(CS) (a) before and (b) after tensile testing.

1D WAXD figures of the three polyesters before and after tensile testing are show in **Figure S7**. Specimens after tensile testing were prepared by stretching the three polymers to a strain of 25 mm/mm and fixed. The middle part of the stretched specimen was characterized by WAXD. Peak fitting of the figures before tensile testing was done by using Origin 9.0 as shown in **Figure S8**, and the degree of crystallinity was calculated. The crystal peak after tensile testing is broader than that before tensile testing, indicating the reduced crystal size. Peak fitting for specimens after tensile testing is difficult to perform, thus the degree of crystallinity is unknown.

8. Peak fitting of 1D WAXD figures

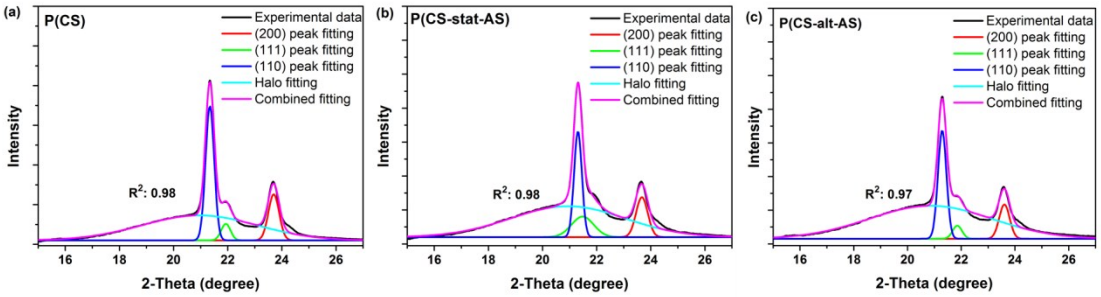


Figure S8. Peak fitting of 1D WAXD figures for (a) P(SC), (b) P(CS-stat-AS) and (c) P(CS-alt-AS).

9. Calculation of Herman's orientation factor

The unit cell structure of crystal is orthorhombic with a, b and c equaling to 7.48, 4.98. 17.26 Å, respectively.[1] Two diffraction patterns at 2θ=21.4 ° and 23.7 ° are observed in the 2D WAXD image, which are assigned to (110) and (200) plane, respectively.[2] The two strong patterns are concentrated from isotropic rings into arcs after stretching due to the orientation of PCL crystals, thus the c* axis of crystal tends to be oriented along the stretching direction (Z direction) during the stretching of the film. However, the diffraction pattern of (002) plane is weak to be observed, so the calculations below are needed to obtain the Herman's orientation factor ($f_{c,\,z}$) of crystal.

Assuming that the crystal is orientated with an angle (∠ZOC) between Z direction and c* axis as shown in **Scheme S1**[2], so the Herman's orientation factor orientation factor ($f_{c,\,z}$) can be calculated in the following equation:

$$f_{(c,\ Z)} = 1/2[3\cos^2(\angle ZOC) - 1]$$

In order to calculate the value of ∠ZOC angle, a line perpendicular to the a*b* plane is drawn with the intersection point of B, and the lines AB and BD are drawn perpendicular to the a* axis and the vector of (110) plane as shown in **Scheme S1**.

The value of ∠ZOC angle can be calculated according to the mathematical relationships[2] below:

$cos\angle ZOA = cos\angle ZOB * cos\angle AOB$

$cos\angle ZOD = cos\angle ZOB * cos\angle BOD$

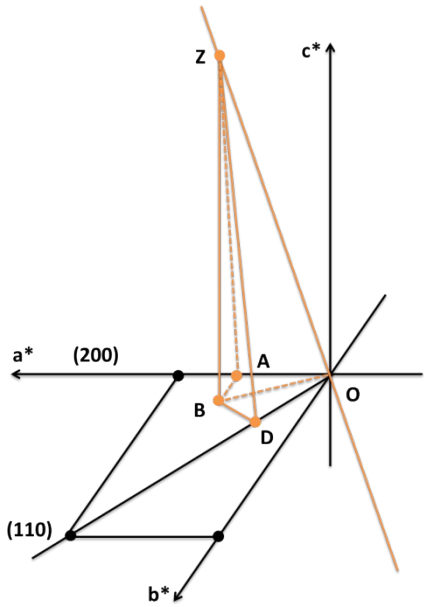
$\angle AOD = \angle AOB + \angle BOD$

$\angle ZOC = 90^\circ - \angle ZOB$

where the angles ∠ZOA and ∠ZOD representing the respective angles of the normal of (200) and (110) plane tilted away from the Z direction can the deduced from their azimuthal profiles. The ∠ZOA angle is 56.4°, representing the dihedral angle between (200) and (110) plane. The calculated values for ∠BOD, ∠ZOC and Herman's orientation factor ($f_{c,z}$) are shown in the Table below:

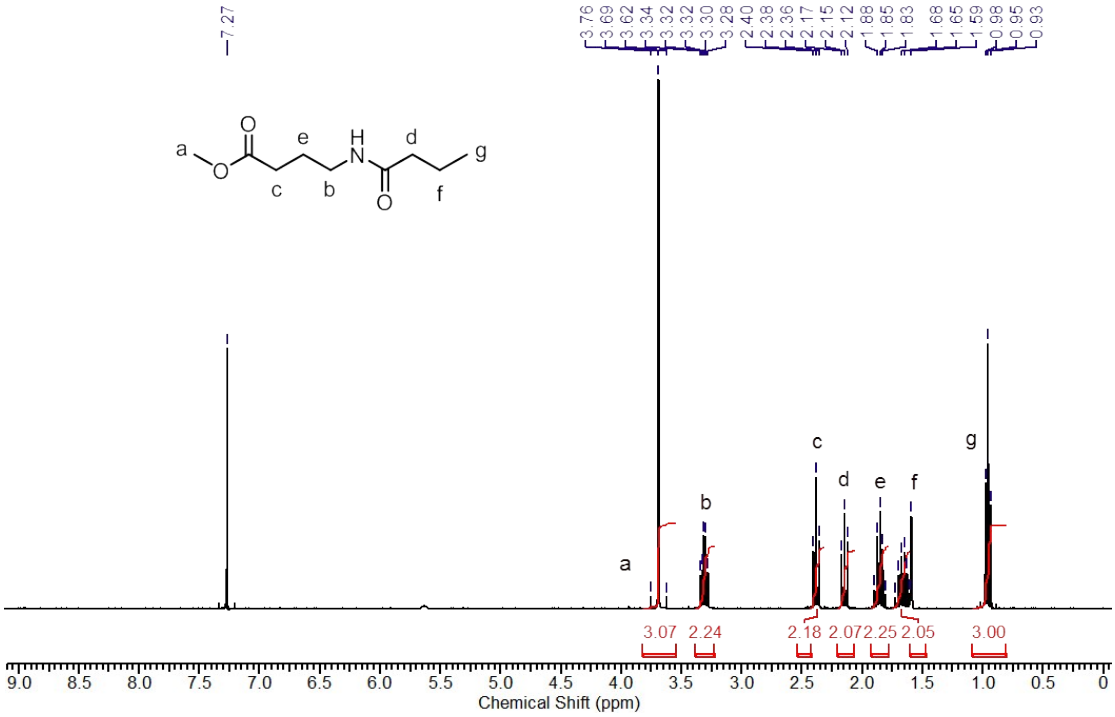
Table S1. Calculation of Herman's orientation factor

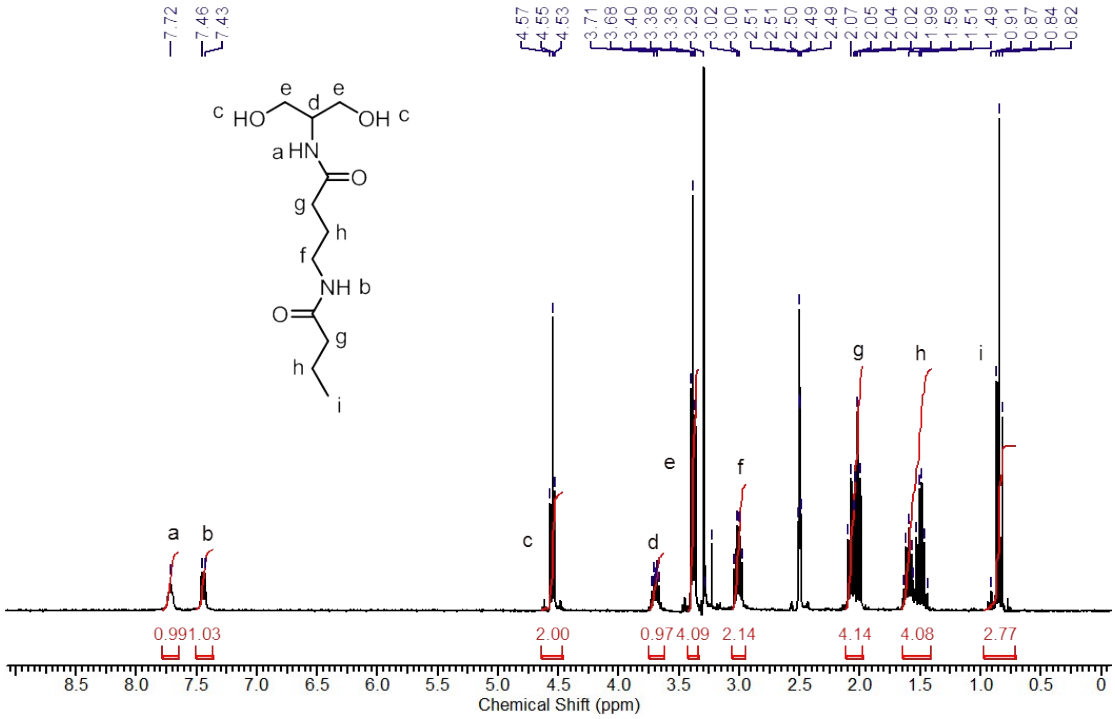
	P(CS)	P(CS-stat-AS)	P(CS-alt-AS)
∠BOD (°)	60.81	51.34	52.14
∠ZOC (°)	20.85	28.68	22.34
$f_{c,z}$	0.81	0.65	0.78

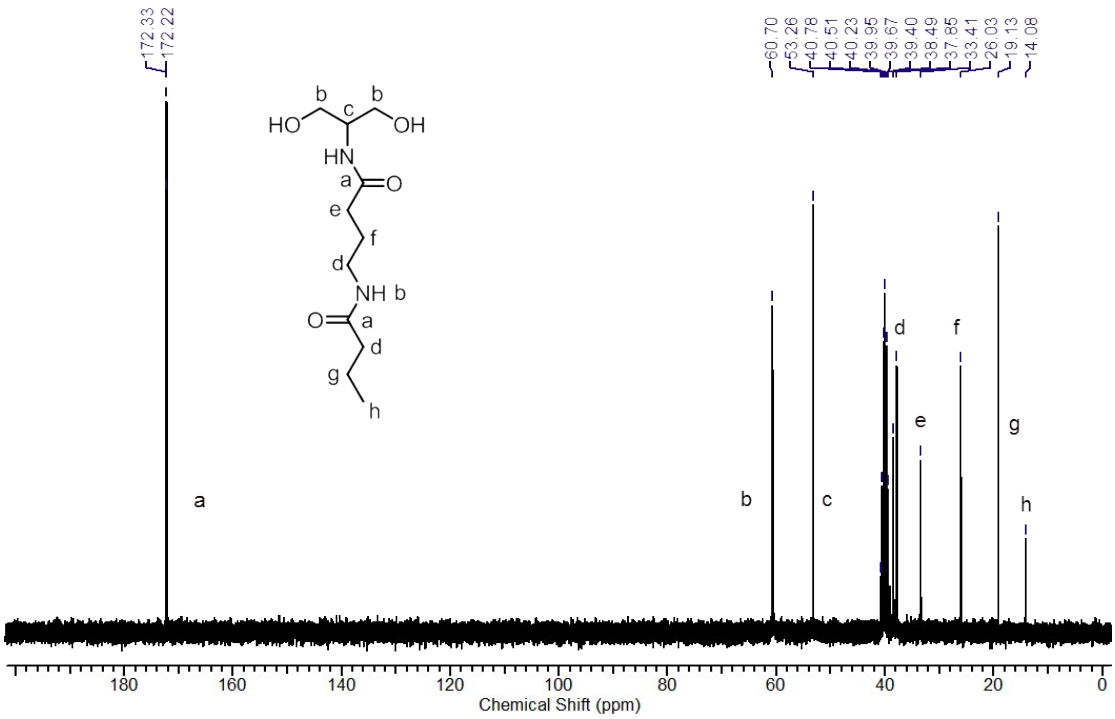


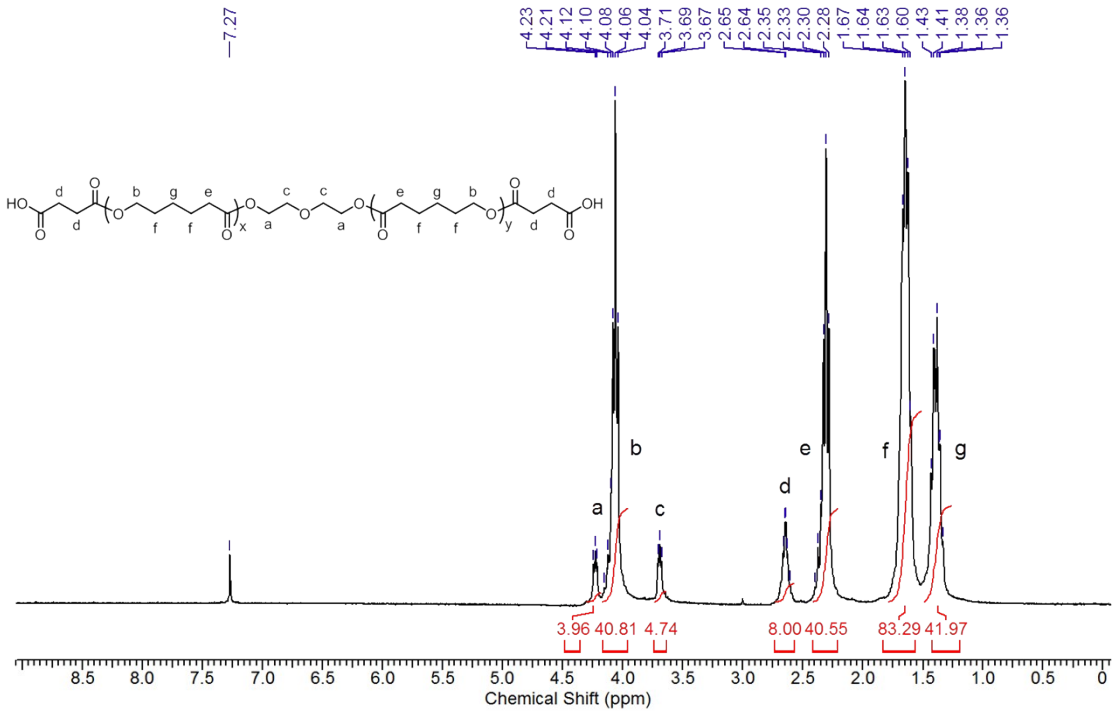
Scheme S1. Schematic of the relationship between Z direction and the reciprocal lattice of crystal.

10. NMR spectra for the pre-monomers and monomers









11. Reference

1. H. Hu and D. L. Dorset, *Macromolecules*, 1990, **23**, 4604-4607.

2. X.-b. Liu, Y.-f. Zhao, X.-h. Fan and E.-q. Chen, *Chinese Journal of Polymer Science*, 2013, **31**, 946-958.