Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Toughened PLA-b-PCL-b-PLA Triblock Copolymer based Biomaterials: Effect of Self-Assembled Nanostructure and Stereocomplexation on the Mechanical Properties

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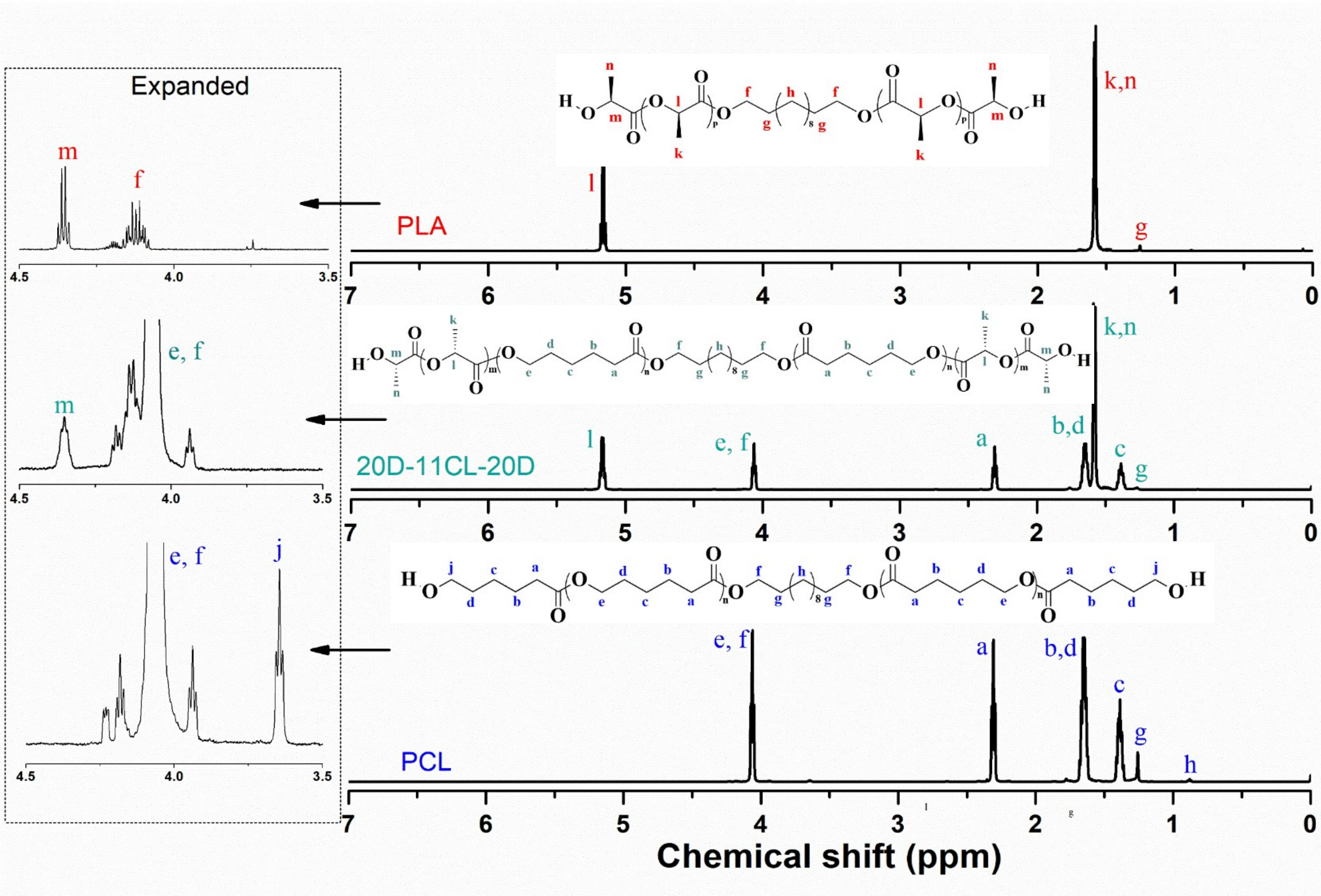

Figure S1: [1]H-NMR spectra of homopolymers and the 20D-11CL-20D triblock copolymer

*The number average molecular weight (Mn) of the homopolymers/block copolymers is determined from ^{1}H-NMR (Figure S1) by using the following equations (S1-i to S1-v):

Degree of polymerization of dihydroxyl terminated PCL, $DP_{PCL} = \frac{e}{j} + 2$ (S1-i)

Degree of polymerization of dihydroxyl terminated PLA, $DP_{PLA} = \frac{l}{m} + 2$ (S1-ii)

Number average molecular weight of dihydroxyl terminated PCL,

$$Mn_{PCL} = (Mo_{PCL} \times DP_{PCL} \times 2) + Mo_{DMG}$$

$$= [114.14 \times \left(\frac{e}{j} + 2\right) \times 2] + 202.34 \qquad \text{(S1-iii)}$$

Number average molecular weight of dihydroxyl terminated PLA,

$$Mn_{PLA} = (Mo_{PLA} \times DP_{PLA} \times 2) + Mo_{DMG}$$

$$= \left[72 \times \left(\frac{l}{m} + 2\right) \times 2\right] + 202.34 \quad \text{(S1-iv)}$$

Number average molecular weight of triblock copolymer (PLA-PCL-PLA)

$$Mn_{triblock} = [(Mo_{PCL} \times DP_{PCL}) + Mo_{DMG}] \; + \; [(Mo_{PLA} \times DP_{PLA} \times 2) + Mo_{DMG}]$$

$$= \left[\left\{114.14 \times \left(\frac{e}{j} + 2\right) \times 2\right\} + 202.34\right] \; + \; \left[\left\{72 \times \left(\frac{l}{m} + 2\right) \times 2\right\} + 202.34\right] \quad \text{(S1-v)}$$

$where,\; Mo$ = molar mass of repeating unit

M_{DMG} = molar mass of initiator

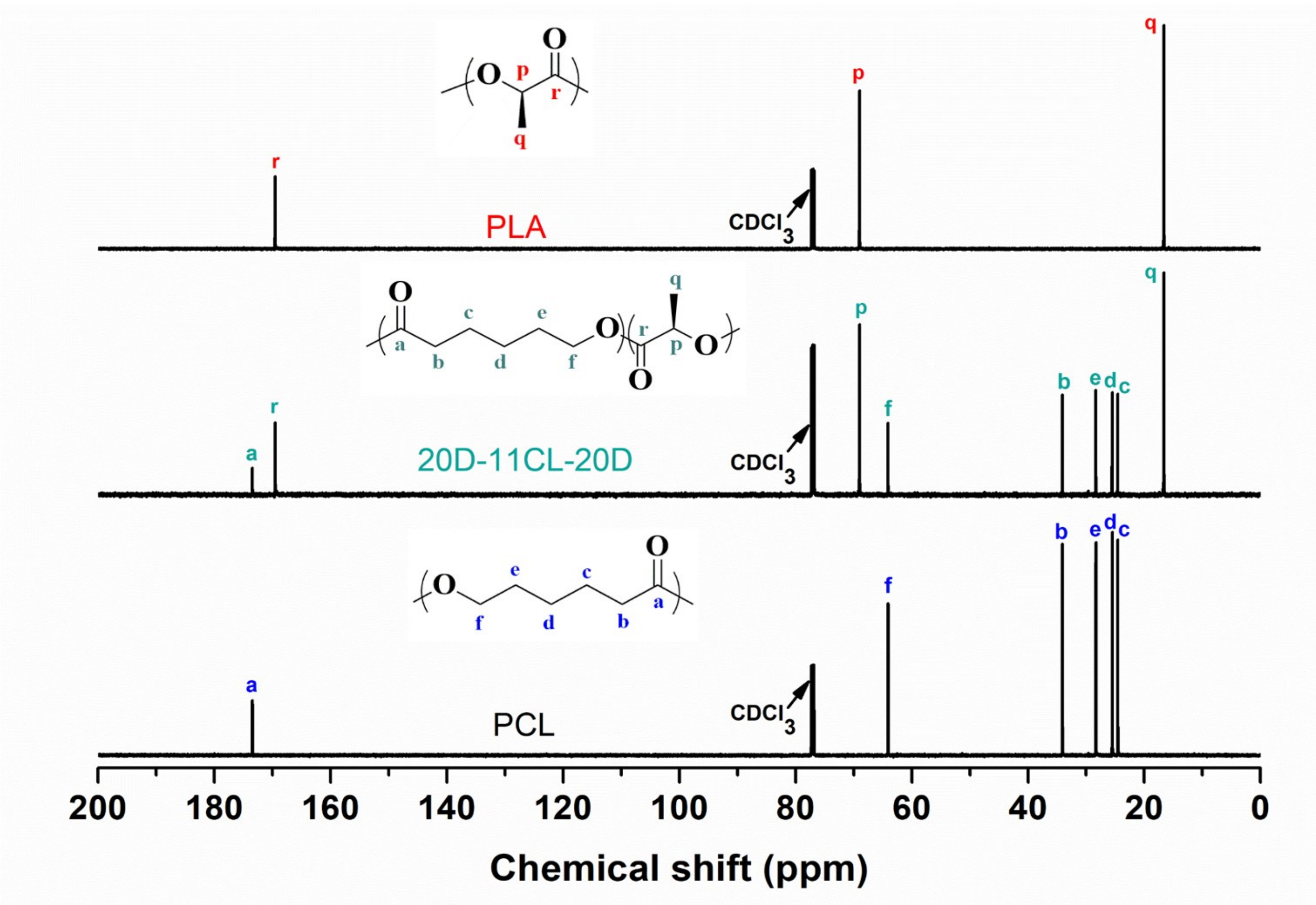

Figure S2: ^{13}C-NMR spectra of homopolymers and the 20D-11CL-20D triblock copolymer

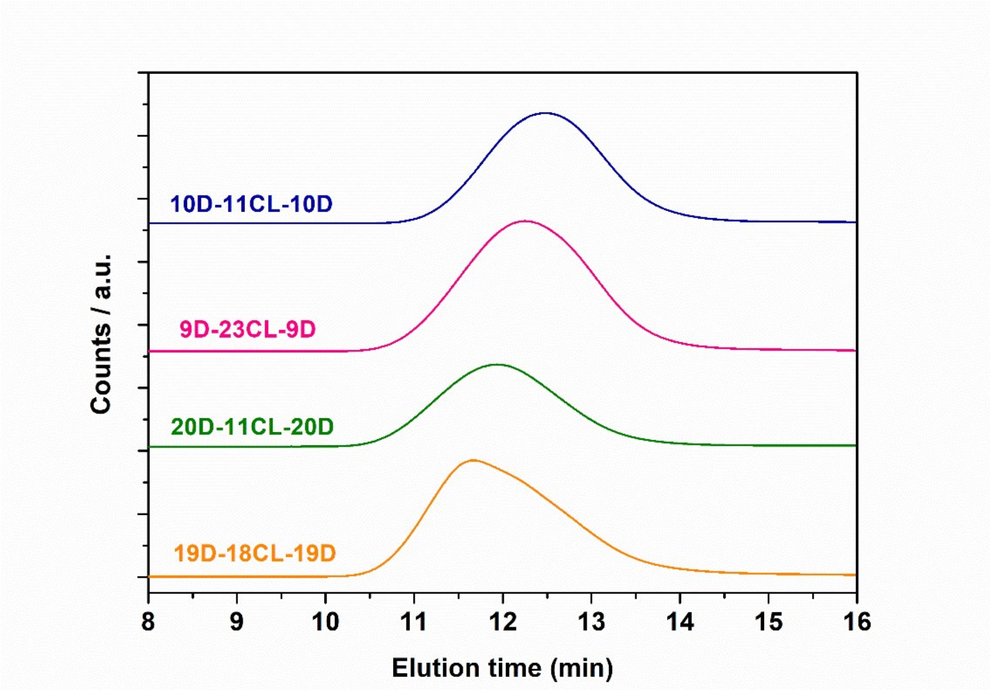

Figure S3: GPC curves of triblock copolymers

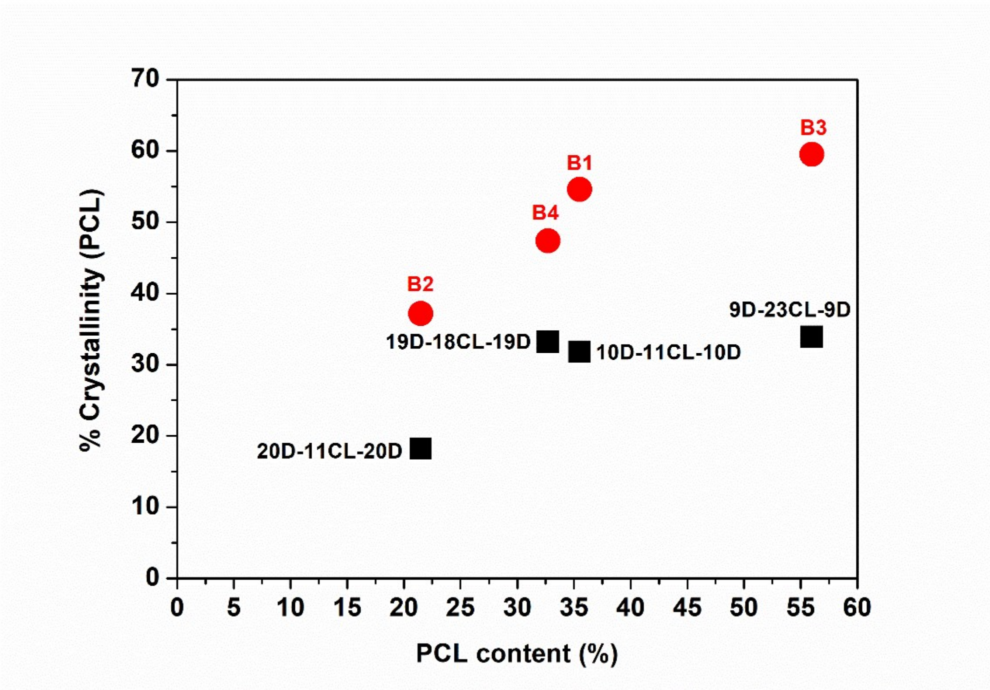

Figure S4: Normalized crystallinity of PCL in the triblock copolymers and blend specimens as determined from WAXS results. Note that this crystallinity can be considered as the normalized one with respect to the PCL content.

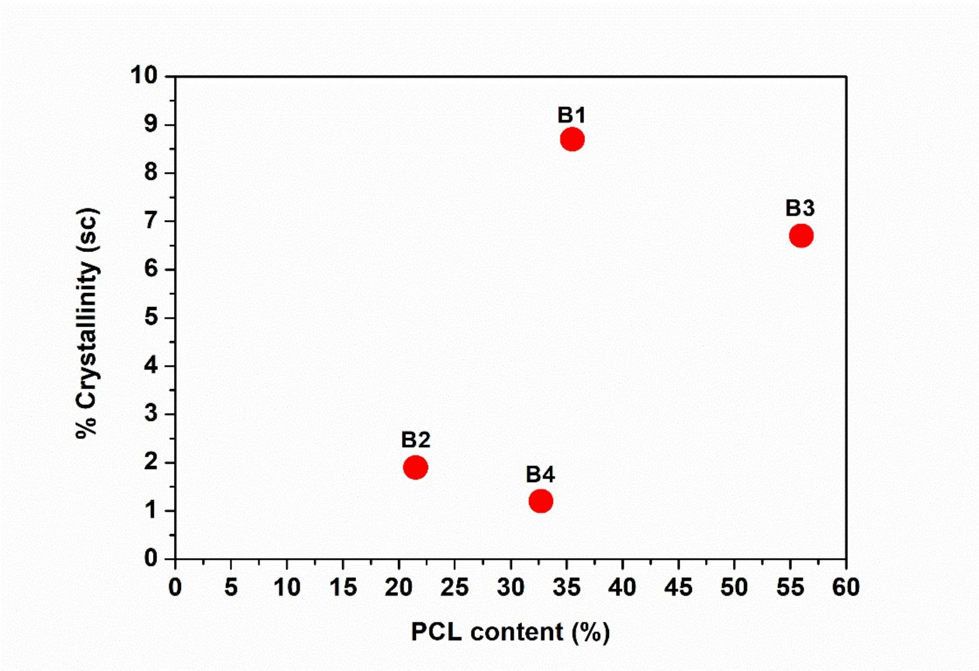

Figure S5: Normalized crystallinity of sc (stereocomplex crystallites) in the blend specimens as determined from WAXS results. Note that this crystallinity can be considered as the normalized one with respect to the sc content.

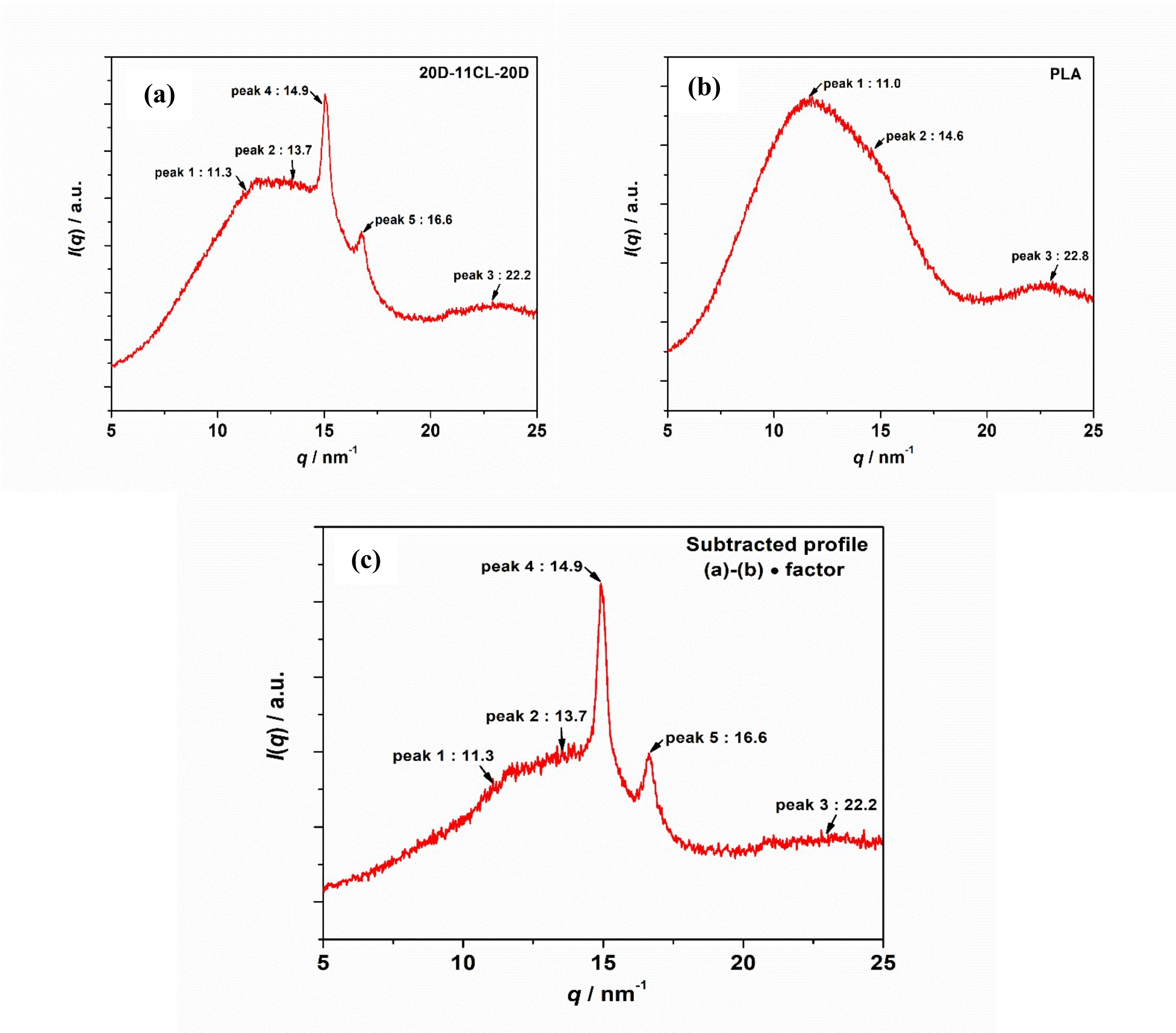

Figure S6: WAXS profiles for (a) the specimen 20D-11CL-20D and (b) PLA homopolymer. The panel (c) indicates subtracted profile. Note here that the amorphous halo of PLA (b) showing peaks at 11.0, 14.6 and 22.8 nm^{-1} was subtracted from the WAXS profile for the triblock copolymer 20D-11CL-20D (a) to completely remove the contribution of amorphous halo due to PLA to yield (c), where the peaks 11.3, 13.7 and 22.2 nm^{-1} are assigned to the amorphous halo of PCL, whereas, the diffraction peaks are observed at 14.9 and 16.6 nm^{-1}. Namely (c) = (a) – (b) • factor and the factor was estimated as follows:

The WAXS profile of PLA (b) was subtracted from that of 20D-11CL-20D (a) such that there was no overestimation of the subtraction which would lead to the negative value of the scattering intensity.

As the content of PLA was 79% in 20D-11CL-20D specimen, the subtraction factor was chosen as 0.8 so as to give (c) = (a) – (b) • 0.8, which would remove completely the amorphous halo of PLA. The factor was adjusted until the complete removal of amorphous PLA halo was achieved.

The similar method was used to completely remove the amorphous halo of PLA for the other specimens.

Table S1: Summaries of the DSC results

Specimen code name	$T_{m,\ PCL}$ (ºC)	$\Delta H_{m,\ PCL}$ (J/g)	$T_{cc,\ PDLA}$ (ºC)	$\Delta H_{cc,\ PDLA}$ (J/g)	$T_{m,\ PDLA}$ (ºC)	$\Delta H_{m,\ PDLA}$ (J/g)	$T_{m,\ scPLA}$ (ºC)	$\Delta H_{m,\ scPLA}$ (J/g)
50D	-	-	103.6	41.3	175.4	49.8	-	-
10D-11CL-10D	54.5	34.3	72.8	13.8	169.8	36.6	-	-
20D-11CL-20D	53.8	11.9	83.3	24.7	173.2	38.9	-	-
9D-23CL-9D	59.5	43.0	68.1	4.5	169.4	27.5	-	-
19D-18CL-19D	56.6	33.5	77.6	21.8	174.5	38.0	-	-
50CL	64.2	78.8	-	-	-	-	-	-
B1 [1)]	53.5	23.5	-	-	167.2	3.9	221.5	45.3
B2 [2)]	54.0	17.3	94.7	18.8	172.8	27.7	222.0	25.3
B3 [3)]	59.5	52.9	-	-	168.3	8.6	218.2	22.0
B4 [4)]	59.2	39.3	99.8	17.3	170.4	15.6	219.8	32.5

[1)] 10D-11CL-10D/10L-11CL-10L (50/50) blend specimen
[2)] 20D-11CL-20D/20L-10CL-20L (50/50) blend specimen
[3)] 9D-23CL-9D/8L-20CL-8L (50/50) blend specimen
[4)] 19D-18CL-19D/16L-22CL-16L (50/50) blend specimen

Crystallinity of PCL from DSC:

$$X_{c,PCL}\,(\%) = \frac{\Delta H_{m,PCL}}{\Delta H^{\circ}_{m,PCL} \times W_{PCL}} \times 100 \qquad \text{(S4-i)}$$

wherse, $\Delta H^{\circ}_{m,PCL}$ = 139.5 J/g and

W_{PCL}= weight fraction of PCL

Table S2: Summaries of the stress-strain results

Specimen code name	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Tensile toughness (MJ/m^3)
50D	39.7 ± 1.9	39.7 ± 1.9	6.8 ± 2.0	1387.2 ± 83.4	2.0 ± 0.7
10D-11CL-10D	12.9 ± 0.8	12.9 ± 0.8	544.7 ± 91.2	508.2 ± 91.9	51.5 ± 12.3
20D-11CL-20D	36.2 ± 1.4	36.2 ± 1.4	708.3 ± 199	792.7 ± 74.4	160.3 ± 19.9
9D-23CL-9D	15.9 ± 3.2	15.9 ± 3.2	598.5 ± 151	677.5 ± 62	69.3 ± 29.4
19D-18CL-19D	21.1 ± 0.6	21.3 ± 0.8	949.6 ± 70.9	580.2 ± 57.9	147.3 ± 16.3
B1 [1)]	9.9 ± 0.8	15.6 ± 1.4	540.6 ± 58	345.6 ± 54	65.4 ± 11.6
B2 [2)]	32.5 ± 3.1	32.5 ± 3.1	661.2 ± 121.5	830.1 ± 56.1	152.9 ± 22.3
B3 [3)]	13.8 ± 1.3	13.8 ± 1.3	430.5 ± 42	602.5 ± 72	38.5 ± 8.7
B4 [4)]	20.1 ± 2.4	20.1 ± 2.4	455.3 ± 37.3	813.3 ± 130.8	70.4 ± 7.8
50CL	13.1 ± 0.8	26.9 ± 1.6	1683 ± 79.4	143.6 ± 19.7	273.4 ± 19.7

[1)] 10D-11CL-10D/10L-11CL-10L (50/50) blend specimen

[2)] 20D-11CL-20D/20L-10CL-20L (50/50) blend specimen

[3)] 9D-23CL-9D/8L-20CL-8L (50/50) blend specimen

[4)] 19D-18CL-19D/16L-22CL-16L (50/50) blend specimen

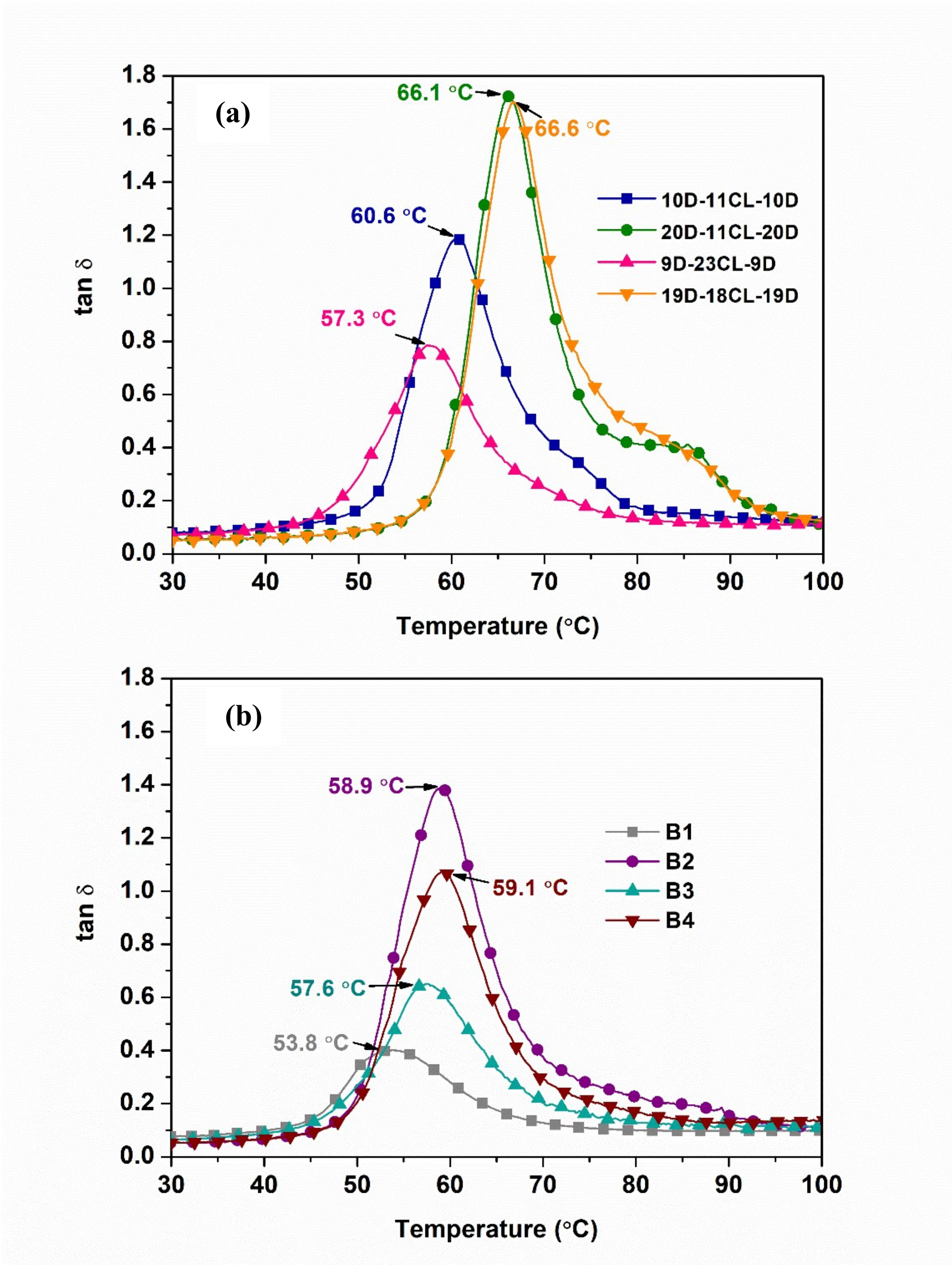

Figure S7: Plots of tan δ vs Temperature (°C) for (a) the neat triblock copolymers and (b) enantiomeric blends, as determined from dynamic mechanical analysis

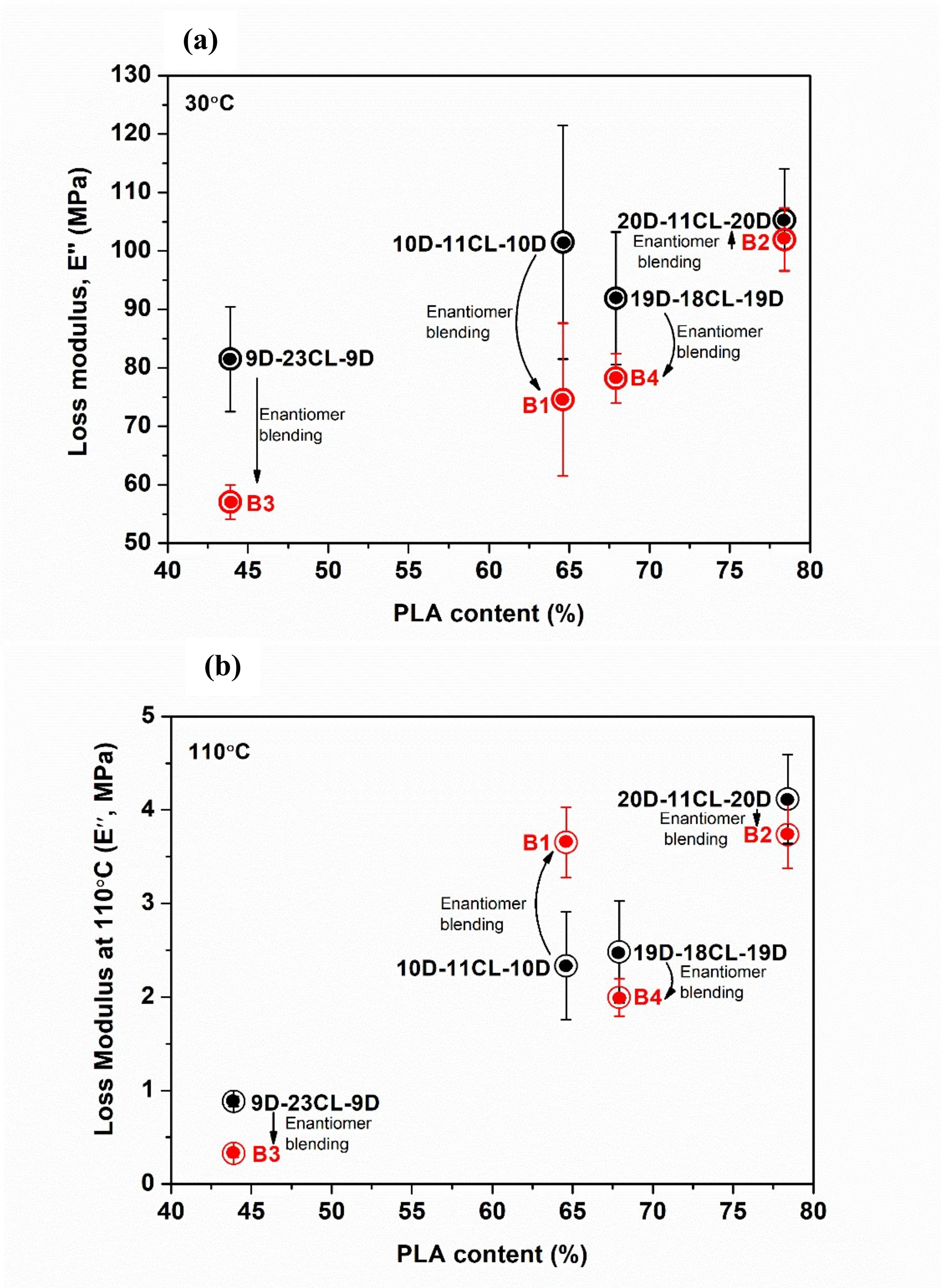

Figure S8: Representative plots of E″ vs PLA content (%) at (a) 30 ℃ and (b) 110 ℃, for the neat triblock copolymers and enantiomeric blends, as determined from dynamic mechanical analysis

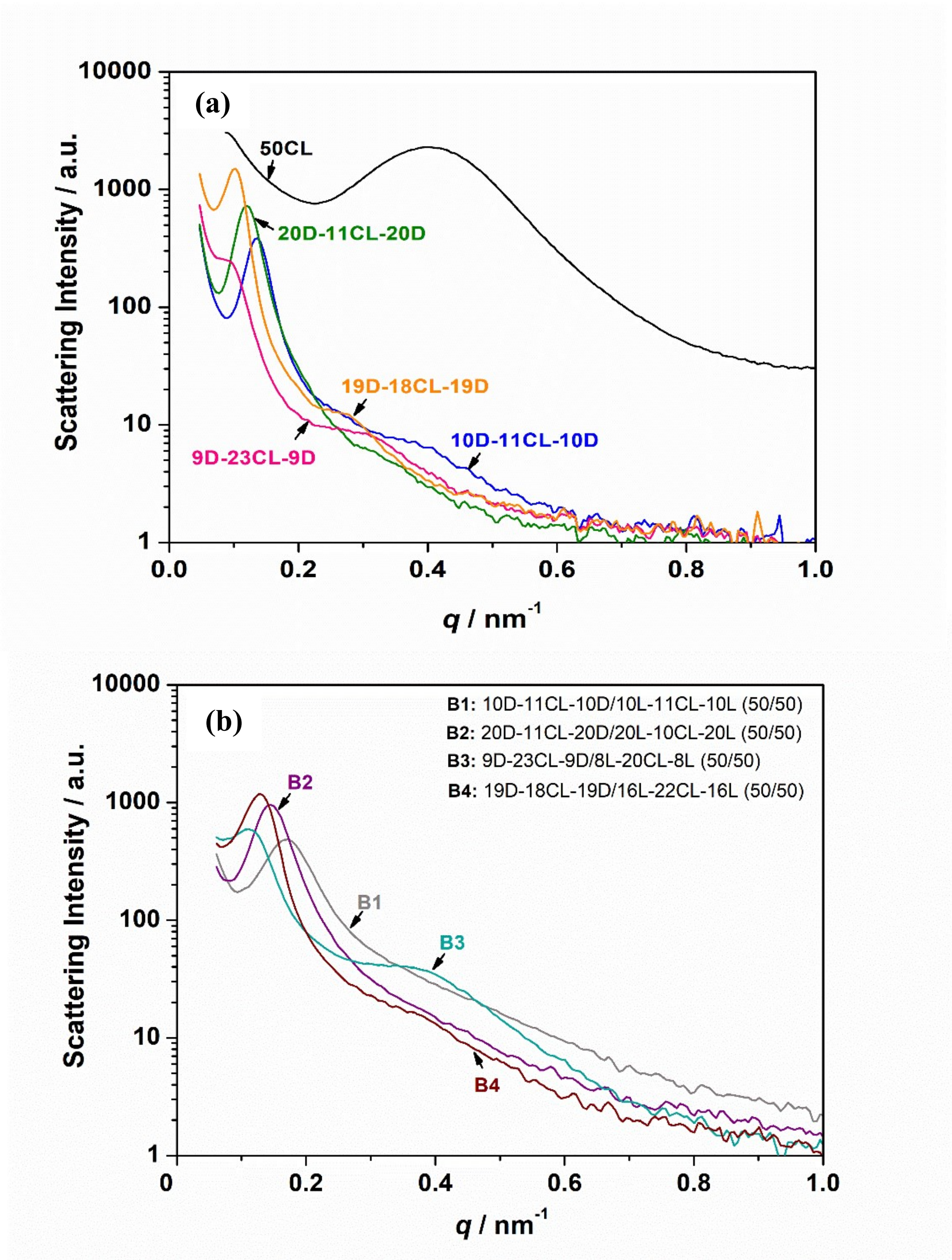

Figure S9: 1d SAXS profiles of (a) neat triblock copolymers and (b) triblock copolymer blends (as-prepared specimens).

Table S3: *d*-spacing of the microdomains and long period of the PCL crystalline lamellar stacking for the neat block copolymers and their blends, as evaluated from SAXS results

Specimen code name	*d*-spacing of the microdomains, (nm)	Long period of the PCL crystalline lamellar stacking, (nm)
50CL	15.8	-
10D-11CL-10D	45.9	15.5
20D-11CL-20D	52.5	19.6
9D-23CL-9D	63.9	19.6
19D-18CL-19D	61.3	22.6
B1 [1)]	36.4	13.6
B2 [2)]	43.5	14.9
B3 [3)]	51.3	16.1
B4 [4)]	46.6	16.6

[1)] 10D-11CL-10D/10L-11CL-10L (50/50) blend specimen
[2)] 20D-11CL-20D/20L-10CL-20L (50/50) blend specimen
[3)] 9D-23CL-9D/8L-20CL-8L (50/50) blend specimen
[4)] 19D-18CL-19D/16L-22CL-16L (50/50) blend specimen

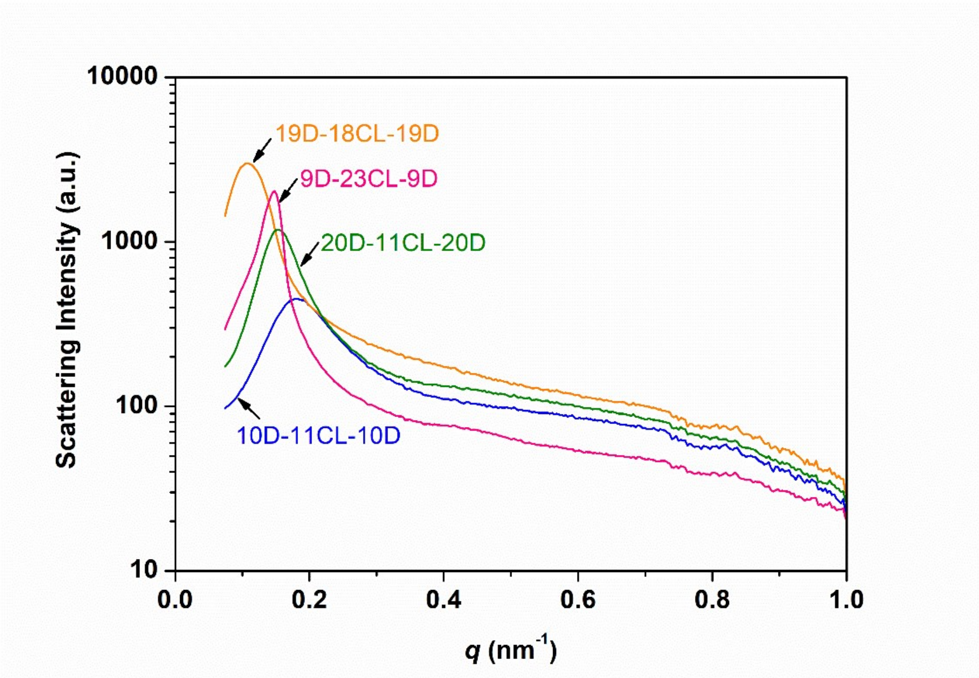

Figure S10: 1d SAXS profiles of the triblock copolymers measured at 210 ℃

Crystallinity of PCL, $X_{c,PCL} = \frac{2l_c}{l_a + 2l_c}$

Table S4: Weight fraction and volume fraction of PCL in the triblock copolymer system

Specimen code name	Weight fraction of PCL	Volume fraction of PCL
10D-11CL-10D	0.35	0.38
20D-11CL-20D	0.21	0.24
9D-23CL-9D	0.56	0.59
19D-18CL-19D	0.32	0.35

$$Weight\ fraction\ of\ PCL = \frac{Weight\ of\ PCL\ block}{Total\ weight\ of\ block\ copolymer} \quad \text{(S13-i)}$$

$$Volume\ fraction = \frac{M_{PCL}/\rho_{PCL}}{M_{PCL}/\rho_{PCL} + M_{PLA}/\rho_{PLA}} \quad \text{(S13-ii)}$$

$\rho_{PCL} = X_c\rho_c + (1 - X_c)\rho_a$, where $\rho_c = 1.2\ g/cc$,[1] $\rho_a = 1.08\ g/cc$ (S13-iii)

$\rho_{PLA} = X_c\rho_c + (1 - X_c)\rho_a$, where $\rho_c = 1.29\ g/cc\{Auras, 2004\ \#34\}$,[2] $\rho_a = 1.25\ g/cc$ (S13-iv)

where M_{PCL} and M_{PLA} denote the molecular weights of PCL and PLA respectively.

References

(1) Crescenzi, V.; Manzini, G.; Calzolari, G.; Borri, C. Thermodynamics of fusion of poly-β-propiolactone and poly-ϵ-caprolactone. comparative analysis of the melting of aliphatic polylactone and polyester chains. *European Polymer Journal* **1972**, *8*, 449-463.

(2) Auras, R.; Harte, B.; Selke, S. An overview of polylactides as packaging materials. *Macromolecular bioscience* **2004**, *4*, 835-864.