*Supplementary Materials*

# Synthesis, Structure, Crystallization and Mechanical Properties of Isodimorphic PBS-*ran*-PCL Copolyesters

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Table S1. Synthesis results of the copolymerization of butylene succinate and ε-caprolactone.

| Polyester | Composition[a] (BS/CL mol/mol) | | Molecular weight[b] (g/mol) | | | Microstructure[c] (S-centered triads content) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Feed | Found | $M_n$ | $M_w$ | $Đ$ | BSB | BSCL/CLSB | CLSCL | $R$ |
| HMw-PBS | 100/0 | 100/0 | 32700 | 70300 | 2.2 | - | - | - | - |
| HMw-$BS_{78}CL_{22}$ | 80/20 | 78/22 | 19750 | 51400 | 2.6 | 62 | 26 | 12 | 1.03 |
| HMw-$BS_{68}CL_{34}$ | 70/30 | 68/32 | 34000 | 91300 | 2.7 | 55 | 28 | 17 | 1.00 |
| HMw-$BS_{60}CL_{40}$ | 60/40 | 60/40 | 18400 | 35500 | 1.9 | 44 | 34 | 22 | 1.10 |
| HMw-$BS_{55}CL_{45}$ | 55/45 | 55/45 | 17300 | 39850 | 2.3 | 48 | 18 | 34 | 0.98 |
| HMw-$BS_{51}CL_{49}$ | 50/50 | 51/49 | 23200 | 87850 | 3.8 | 44 | 14 | 42 | 1.00 |
| HMw-$BS_{46}CL_{54}$ | 45/55 | 46/54 | 26000 | 60700 | 2.3 | 40 | 13 | 47 | 1.02 |
| HMw-$BS_{38}CL_{62}$ | 40/60 | 38/62 | 17800 | 39500 | 2.2 | 29 | 16 | 55 | 1.01 |
| HMw-$BS_{15}CL_{85}$ | 15/90 | 15/85 | 26350 | 53100 | 2.0 | 8 | 14 | 78 | 1.00 |
| HMw-PCL | 0/100 | 0/100 | 31000 | 60000 | 1.9 | - | - | - | - |

[a] Composition of the feed and the resulting polymer as determined by $^1$H NMR.
[b] Number and weight average molecular weights and dispersities estimated by GPC against PMMA standards.
[c] Copolyester microstructure determined by NMR; R is the degree of randomness which should be 1 for a fully statistical distribution of the comonomeric units.
*Polycondensation were performed under vacuum at 220 °C for around 5h.

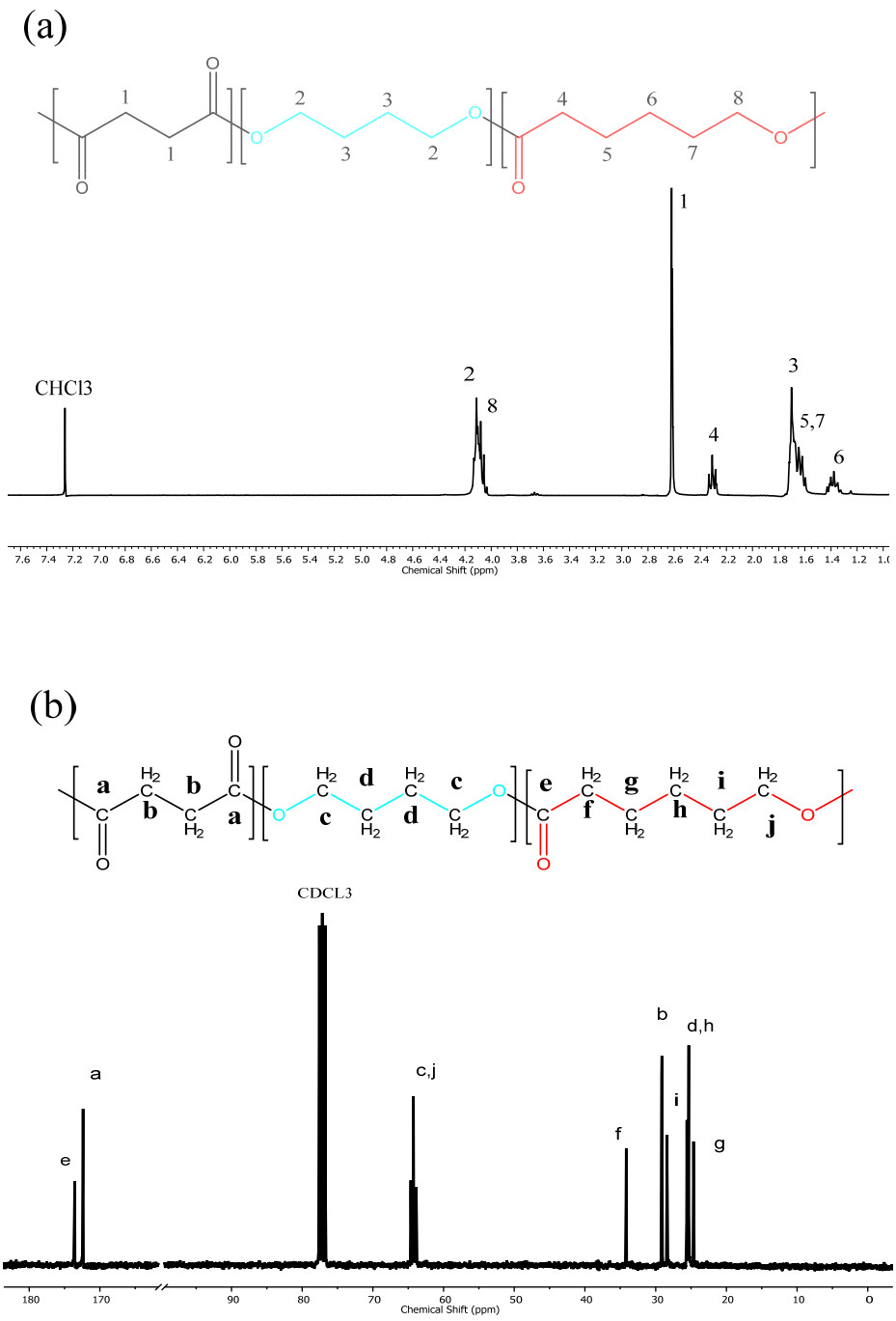


**Figure S1.** $^{1}H$ (a) and $^{13}C$ (b) NMR spectra of HMw-$BS_{51}CL_{49}$ as representative of the HMw-$BS_xCL_y$ copolyesters series recorded in $CDCl_3$. Peaks were assigned according to the expected copolyester constitution depicted in the attached formula.

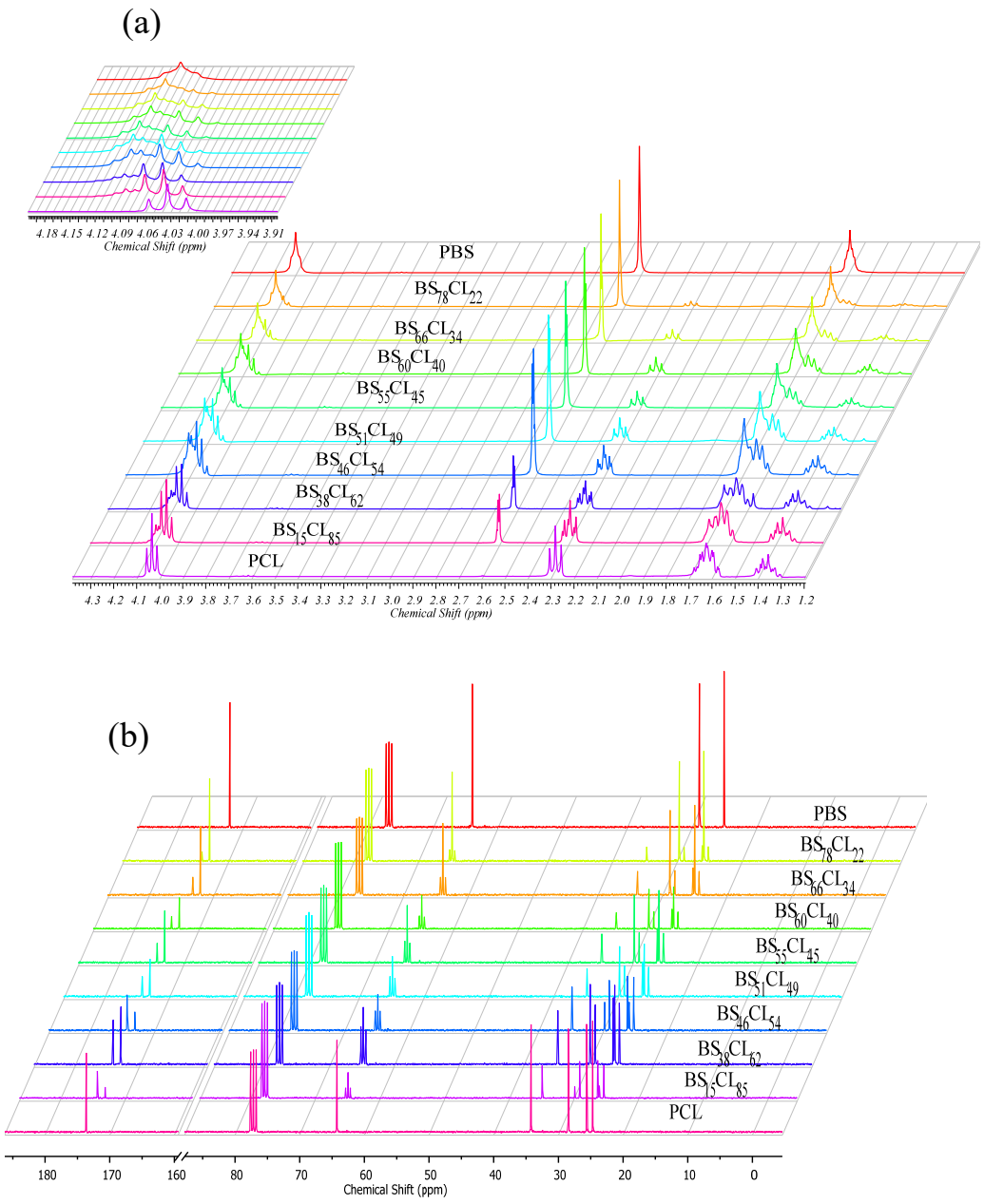


**Figure S2.** $^{1}H$ (a) and $^{13}C$ (b) NMR spectra comparison of all HMw-$BS_xCL_y$ copolyesters series.

**Table S2.** Thermal characterization data of HMw-$BS_xCL_y$ copolymer obtained from DSC.

| Copolymer | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $X_c$ (%) |
|---|---|---|---|---|---|
| HMw-PBS | 114.6 | 66 | 69.2 | 59 | 54 |
| HMw-$BS_{78}CL_{22}$ | 94.1 | 46 | 43.0 | 41 | 30 |
| HMw-$BS_{68}CL_{32}$ | 78.3 | 40 | 13.8 | 8 | 5 |
| HMw-$BS_{60}CL_{40}$ | 69.2 | 38 | 10.8 | 8 | 4.5 |
| HMw-$BS_{55}CL_{45}$ | 67.0 | 35 | 10.1 | 8 | 4 |
| HMw-$BS_{51}CL_{49}$ | 53.8 | 30 | -9.5 | 1.8 | 1 |
| HMw-$BS_{46}CL_{54}$ | 40 & 15 | 17 &24 | -25.0 | 0.9 | 0.5 |
| HMw-$BS_{38}CL_{62}$ | 23.6 | 32 | -3.8 | 35 | 15 |
| HMw-$BS_{15}CL_{85}$ | 31.2 | 42 | 3.2 | 39 | 23 |
| HMw-PCL | 56.8 | 55 | 33 | 55 | 38 |

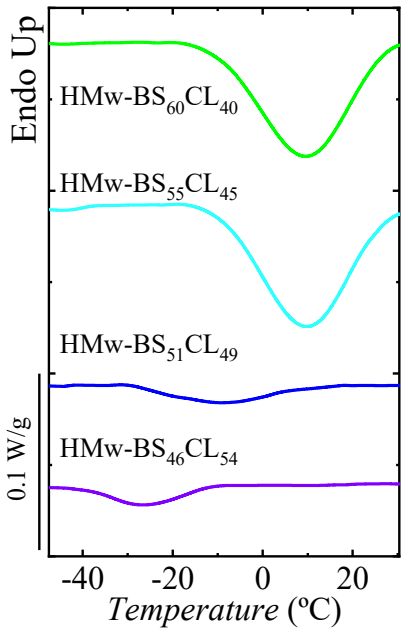


**Figure S3**. Cooling DSC scans from the melt for those compositions that show a broad crystallization peak.

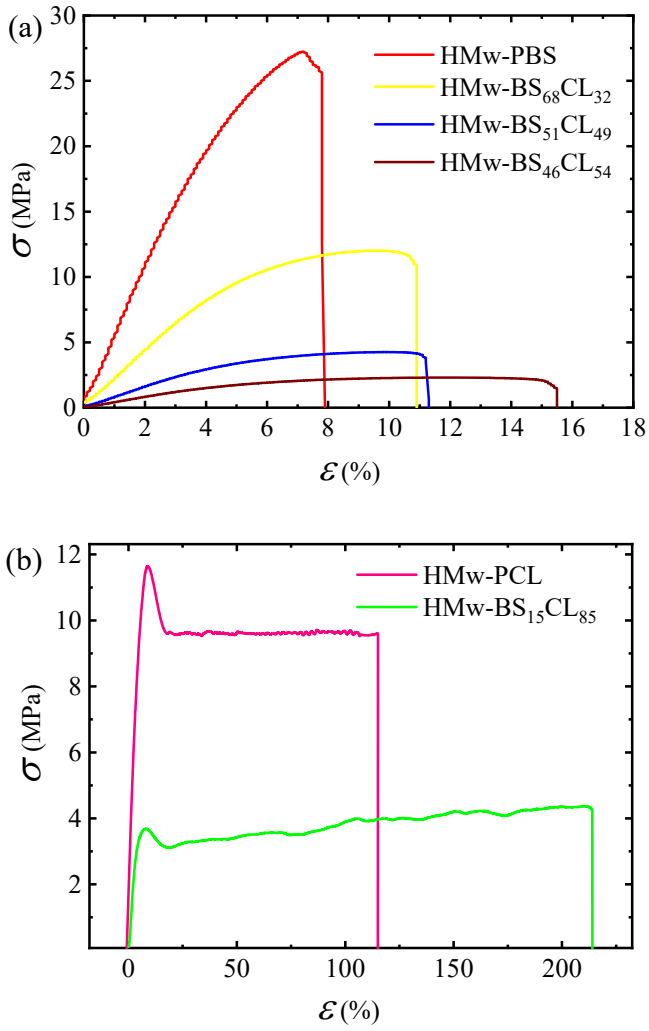


**Figure S4.** Representative stress-strain curves of (a) BS-rich HMw-BS$_x$CL$_y$ and (b) CL-rich HMw-BS$_x$CL$_y$ random copolyesters.

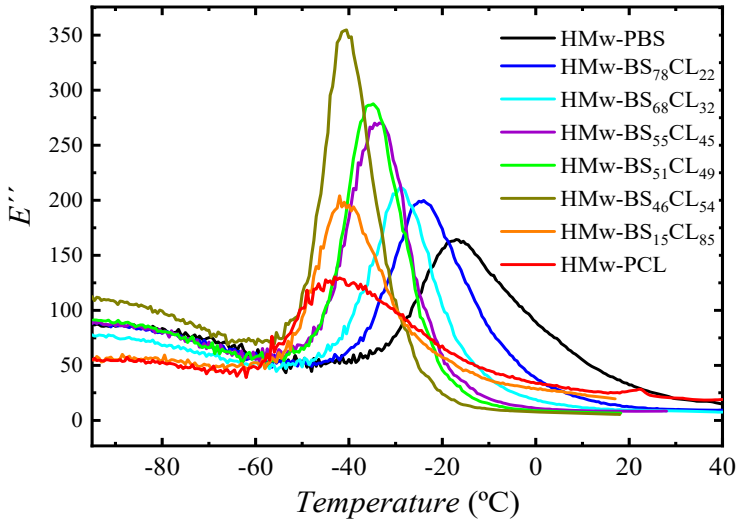


**Figure S5.** Loss modulus as a function of temperature at a constant heating rate of 4 °C/min and frequency of 1 Hz for HMw-$BS_xCL_y$ copolyesters.

**Table S3.** Nucleation and growth constants obtained from isothermal crystallization kinetics of PBS homopolymer and PBS-rich phase compositions obtained by PLOM measurement.

| Copolyester | $K_g^G$ (K²) | $\sigma$ (erg/cm²) | $\sigma_e$ (erg/cm²) | $q$ (erg) | $R^2$ |
|---|---|---|---|---|---|
| **PBS** | 8.66E+04 | 12.36 | 79.52 | 3.37E-13 | 0.983 |
| $\mathbf{BS_{91}CL_9}$ | 5.80E+04 | 12.36 | 55.01 | 2.33E-13 | 0.994 |
| $\mathbf{BS_{78}CL_{22}}$ | 5.12E+04 | 12.36 | 49.55 | 2.10E-13 | 0.973 |
| $\mathbf{BS_{66}CL_{34}}$ | 8.94E+04 | 12.36 | 88.90 | 3.78E-13 | 0.982 |
| $\mathbf{BS_{62}CL_{38}}$ | 8.92E+04 | 12.36 | 89.42 | 3.87E-13 | 0.982 |
| $\mathbf{BS_{55}CL_{45}}$ | 14.4E+04 | 12.36 | 148.8 | 6.30E-13 | 0.999 |
| $\mathbf{BS_{51}CL_{49}}$ | 14.5E+04 | 12.36 | 148.9 | 6.32E-13 | 0.999 |
| $\mathbf{BS_{45}CL_{55}}$ | 15.7E+04 | 12.36 | 165.5 | 7.02E-13 | 0.974 |
| $\mathbf{BS_{11}CL_{89}}$ | 14.7E+04 | 6.83 | 169.58 | 6.32E-13 | 0.999 |
| **PCL** | 10.4E+04 | 6.83 | 111.97 | 4.17E-13 | 0.996 |

$R^2$ is the correlation coefficient for the Lauritzen–Hoffman, linear plots, $\ln(1/\tau_{50\%}) + U^*/R(Tc - T\alpha)$ vs. $1/f{\cdot}Tc{\cdot}\Delta T$.

**Table S4.** Parameters obtained from fitting the DSC data presented in Figure 7 (a-b) to the Lauritzen–Hoffman model.

| Copolyester | $K_g^t$ (K²) | $R^2$ | $\sigma$ (erg/cm²) | $\sigma_e$ (erg/cm²) | $q$ (erg) |
|---|---|---|---|---|---|
| **PBS** | 2.04E+05 | 0.9697 | 12.36 | 186.88 | 7.93E-13 |
| $\mathbf{BS_{91}CL_9}$ | 1.85E+05 | 0.9938 | 12.36 | 173.80 | 3.37E-13 |
| $\mathbf{BS_{78}CL_{22}}$ | 2.44E+05 | 0.9514 | 12.36 | 236.34 | 10.0E-13 |
| $\mathbf{BS_{66}CL_{34}}$ | 2.92E+05 | 0.9958 | 12.36 | 290.42 | 12.3E-13 |
| $\mathbf{BS_{55}CL_{45}}$ | 3.76E+05 | 0.9775 | 12.36 | 387.34 | 16.4E-13 |
| $\mathbf{BS_{51}CL_{49}}$ | 3.79E+05 | 0.9973 | 12.36 | 388.50 | 16.8E-13 |
| $\mathbf{BS_{45}CL_{55}(BS-rich)}$ | 4.91E+05 | 0.9502 | 18.54 | 518.73 | 22.0E-13 |
| $\mathbf{BS_{45}CL_{55}(CL-rich)}$ | 12.5E+05 | 0.9880 | 6.83 | 1376.9 | 51.3E-13 |
| $\mathbf{BS_{38}CL_{62}}$ | 2.66E+05 | 0.9917 | 6.83 | 328.01 | 12.6E-13 |
| $\mathbf{BS_{27}CL_{73}}$ | 2.52E+05 | 0.9845 | 6.83 | 305.91 | 11.4E-13 |
| $\mathbf{BS_{11}CL_{89}}$ | 2.41E+05 | 0.9945 | 6.83 | 278.43 | 10.4E-13 |
| **PCL** | 2.40E+05 | 0.9082 | 6.83 | 260.61 | 9.71E-13 |

$R^2$ is the correlation coefficient for the Lauritzen–Hoffman, linear plots $\ln(1/\tau_{50\%}) + U^*/R(Tc - T\alpha)$ vs. $1/f{\cdot}Tc{\cdot}\Delta T$.