Supporting Information

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PCL-based shape memory polymer semi-IPNs: The role of miscibility in tuning degradation rate

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(a)

Polymer	M_n (kDa) (NMR)	Ratio L:G (NMR)	T_g (°C) (DSC)	T_m (°C) (DSC)	% Cryst (DSC)
PCL-diol	Sigma	-	-65.2 ± 0.98	52.6 ± 0.16	46.5 ± 0.21
7.5k PLLA	8.3	-	44.9 ± 0.93	153.1 ± 0.35	49.3 ± 1.9
15k PLLA	15.1	-	45.1 ± 0.72	155.4 ± 0.35	52.7 ± 0.14
30k PLLA	27.5	-	46.3 ± 2.78	158.8 ± 0.85	56.2 ± 1.4
120k PLLA	Sigma	-	50.4 ± 0.47	170.3 ± 0.22	20.0 ± 1.2
PDLLA	11.3	-	28.4 ± 0.13	-	-
85:15 PLGA	14.2	84:16	41.2 ± 1.49	137.4 ± 6.2	3.17 ± 0.74
70:30 PLGA	12.7	67:33	37.3 ± 2.22	-	-
50:50 PLGA	11.7	49:51	21.1 ± 0.37	-	-

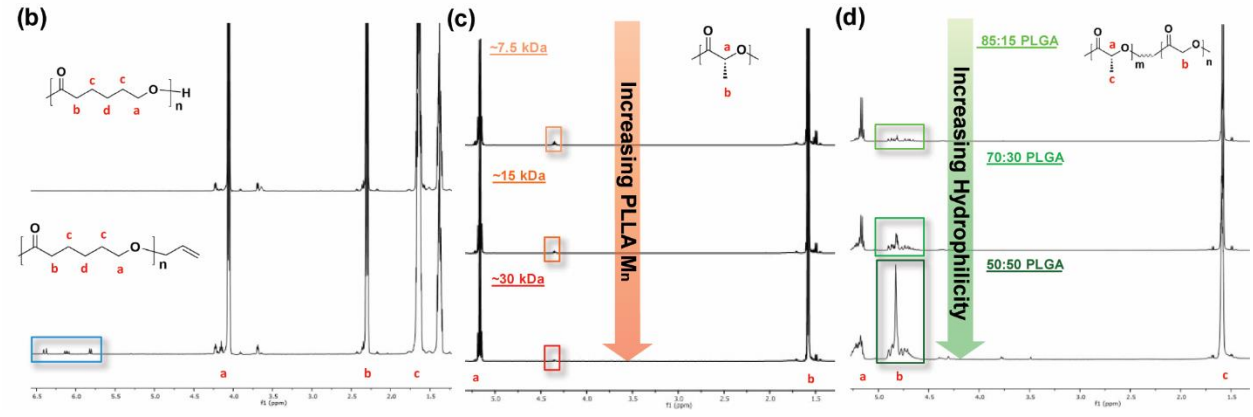


Figure S1. NMR and DSC results for each polymer are summarized in the table (a), stacked NMR showing successful acrylation of PCL [acrylate peaks boxed in blue] (b), stacked NMR showing PLLA with increasing M_n [as reference peak, boxed in orange, decreases] (c) and stacked NMR showing PLGAs with increasing glycolide content [boxed in green] (d).

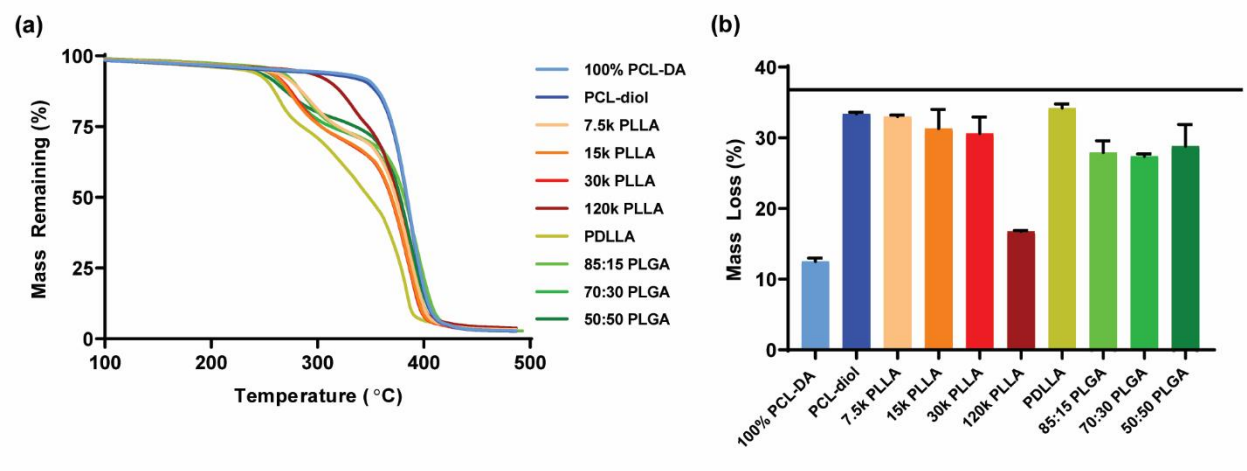
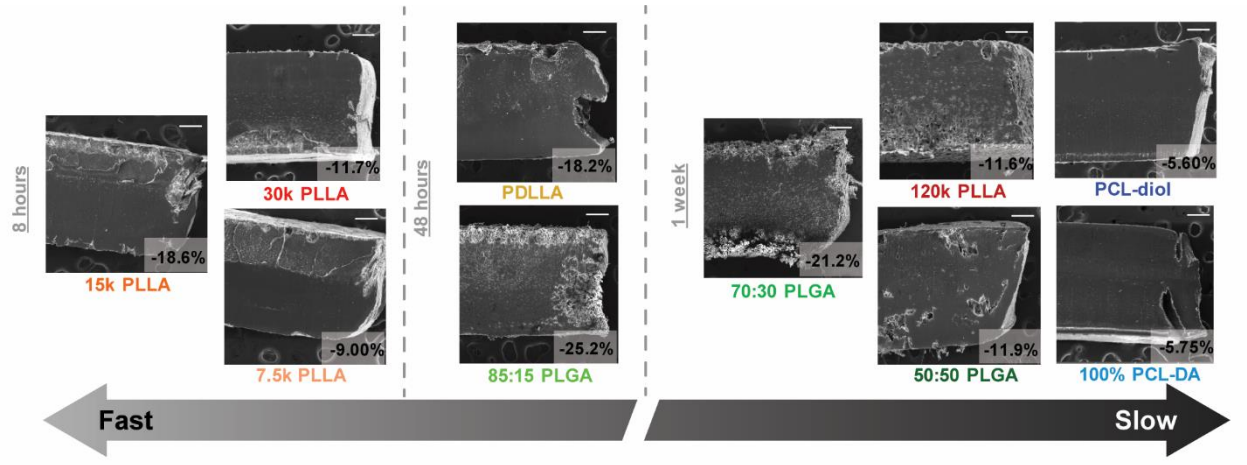


Figure S2. TGA results verifying ~25% thermoplastic in PCL-DA/PLA semi-IPNs (a) and sol content values demonstrating adequate cross-linking with an upper limit of ~37% mass loss [~12% 100% PCL-DA control + ~25% thermoplastic] for semi-IPN films (b).



Figures S3. SEM of degraded film cross-sections at noted timepoints and ranking of PCL-DA/PLA semi-IPNs based on degradation rate. Average mass loss values are noted on the SEM images. Scale bars = 250 µm.

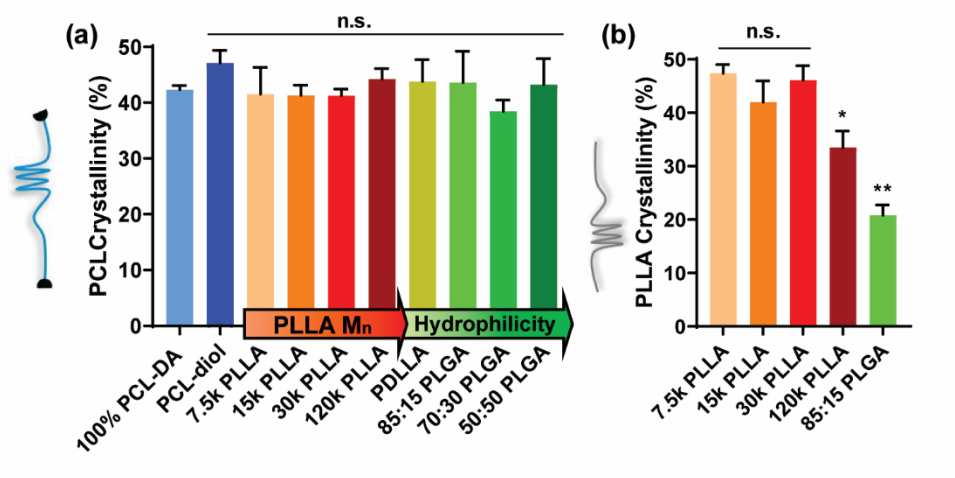


Figure S4. PCL % crystallinity of semi-IPNs was maintained at ~40% (corrected for relative mass percent of PCL-DA in the semi-IPN), *$p < 0.05$ versus the 100% PCL-DA control (a). PLLA % crystallinity of the 120 k PLLA semi-IPN (~33%) was significantly reduced versus that of 7.5 k, 15 k and 30 k PLLA semi-IPNs (~45%). PLLA % crystallinity of the 85:15 PLGA semi-IPN increased to ~20% (versus ~3% for PLGA thermoplastic). *$p < 0.05$ and **$p < 0.01$ versus the 7.5 k PLLA.

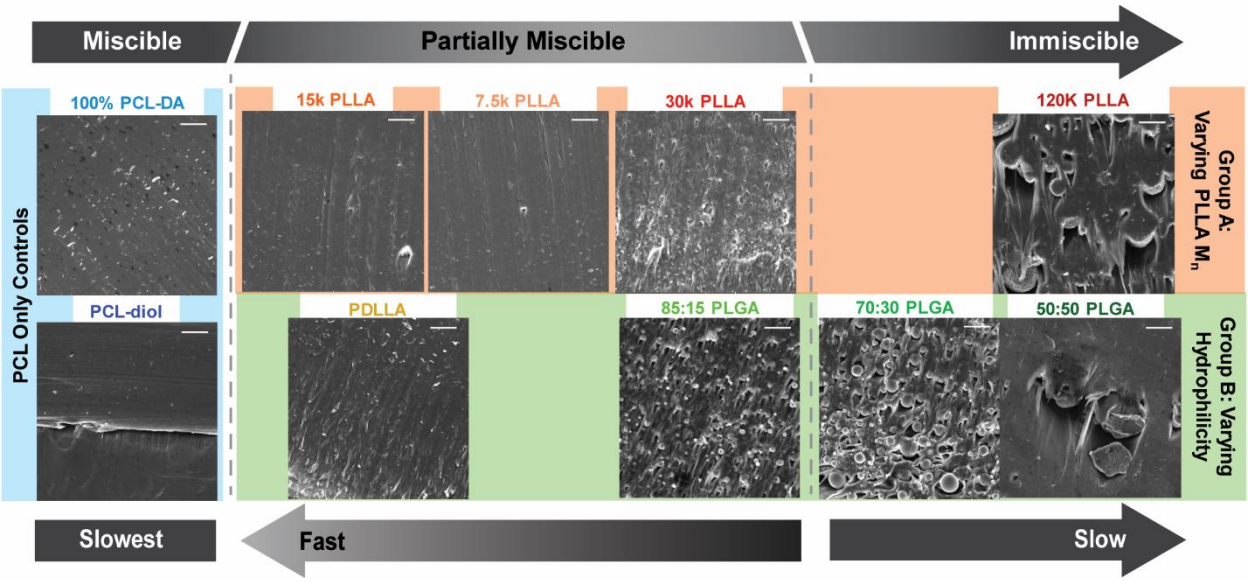


Figure S5. SEM images of semi-IPNs and controls film cross-sections prior to degradation. Categorization of miscibility ("miscible", "partially miscible" or "immiscible") based on extent of phase separation and corresponding relative rate of degradation (slow or fast). Scale bars = 50 µm.

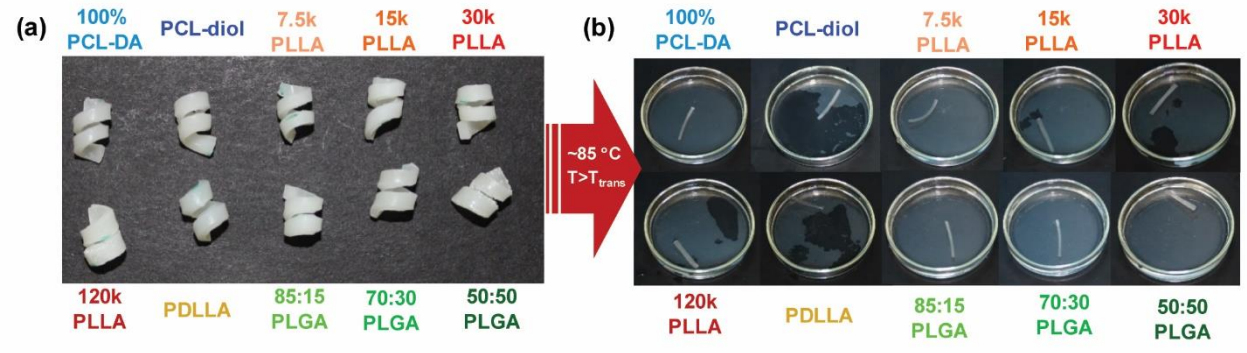


Figure S6. Qualitative shape memory testing was performed and all compositions were able to effectively hold a temporary coil shape (a), and upon heating, all samples returned to their permanent rectangular shape in ~10 sec (b).

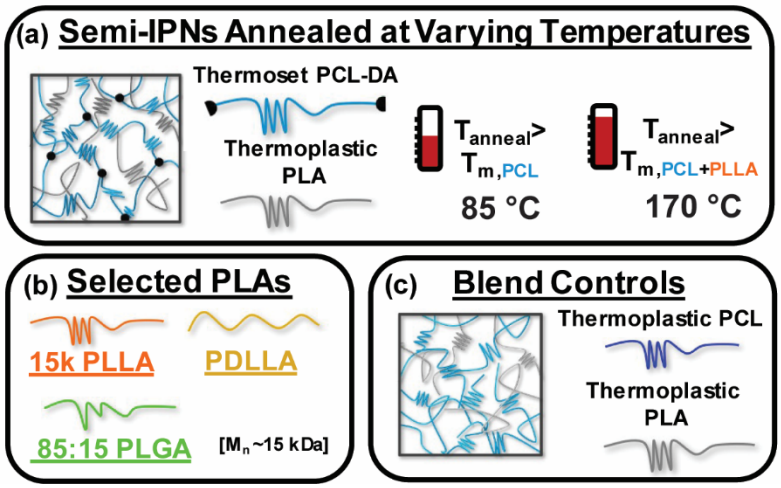


Figure S7. Schematic summarizing the study to assess the impact of increased annealing temperature for selected semi-IPNs (a), PLA thermoplastics used to form the semi-IPNs (b) and blend controls (c).

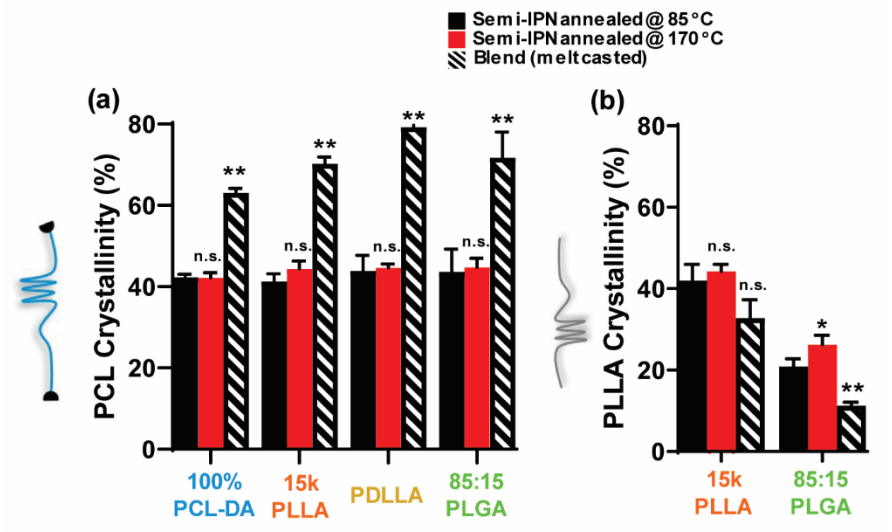


Figure S8. PCL % crystallinity (a) and PLLA % crystallinity (b) in PCL-DA/PLA semi-IPNs and controls annealed at 85 °C and 170 °C and analogous blend controls. Values were corrected for mass percent and PCL % crystallinity was maintained in semi-IPNs annealed at both temperatures but was significantly higher in all blends. *$p < 0.05$ and **$p < 0.01$ versus the corresponding control or semi-IPN annealed at 85 °C (a) and *$p < 0.05$ and **$p < 0.01$ versus the corresponding semi-IPN annealed at 85 °C (b).

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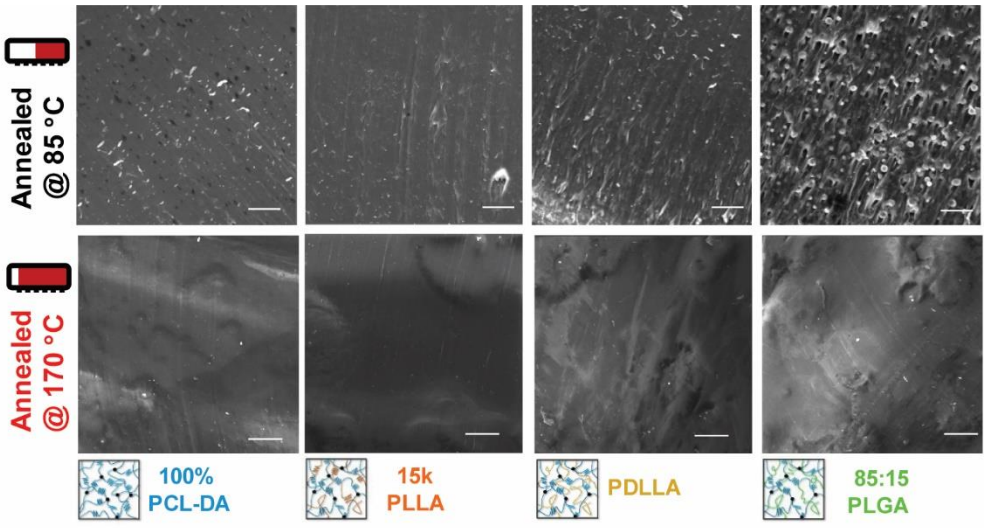

Figure S9. SEM of semi-IPN and control film cross-sections (annealed at 85 °C or 170 °C) prior to degradation. Annealing at the higher temperature reduced phase separation. Scale bars = 50 µm.

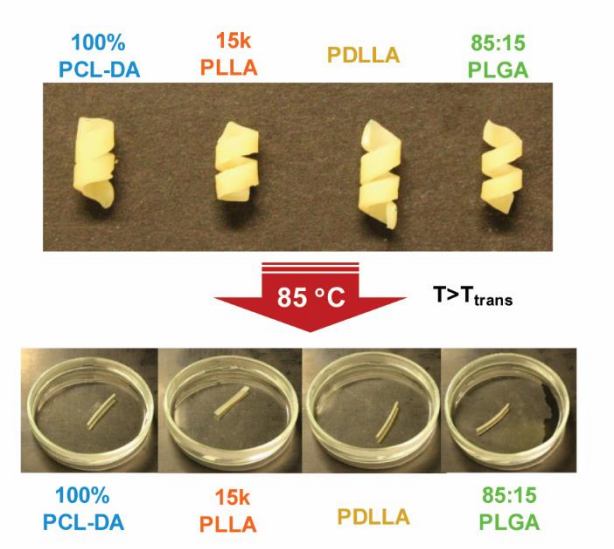

Figure S10. Shape memory properties were visualized qualitatively, and all compositions annealed at 170 °C were shown to maintain shape fixity (a) and shape recovery (b).