Supplementary Information

A Versatile Strategy for Synthesis and Mechanical Property Manipulation of Networked Biodegradable Polymeric Materials Composed of Well-Defined Alternating Hard and Soft Domains

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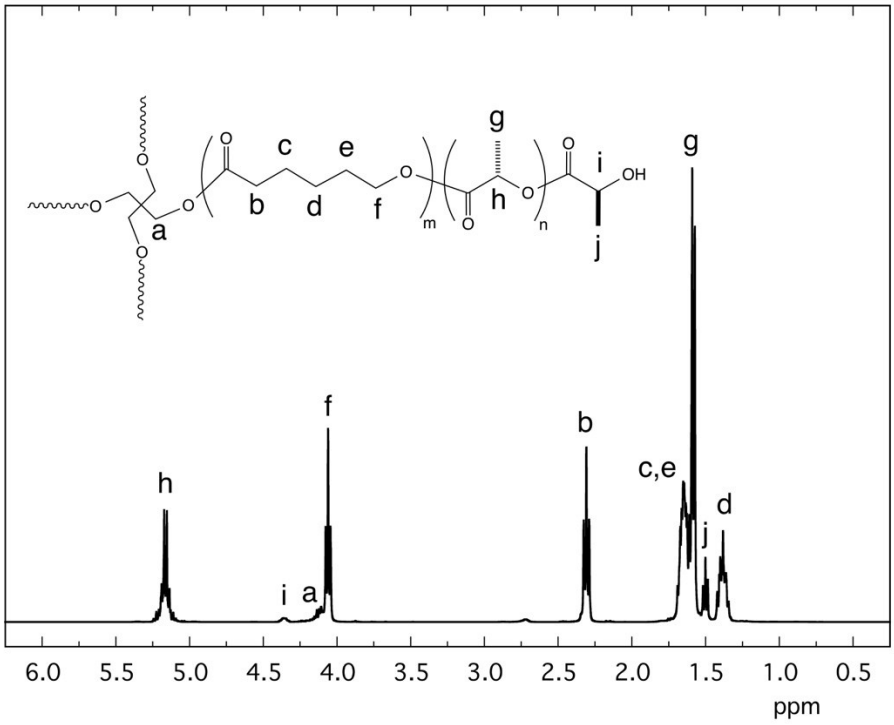

Figure S1. Typical ^{1}H NMR spectrum of 4-C-L copolymer (4-C49-L38).

S2. Typical GPC curves of 4-C and 4-C-L polymers (before and after 2nd step polymerization, 4-C49 and 4-C49-L38, respectively) (Figure S2)

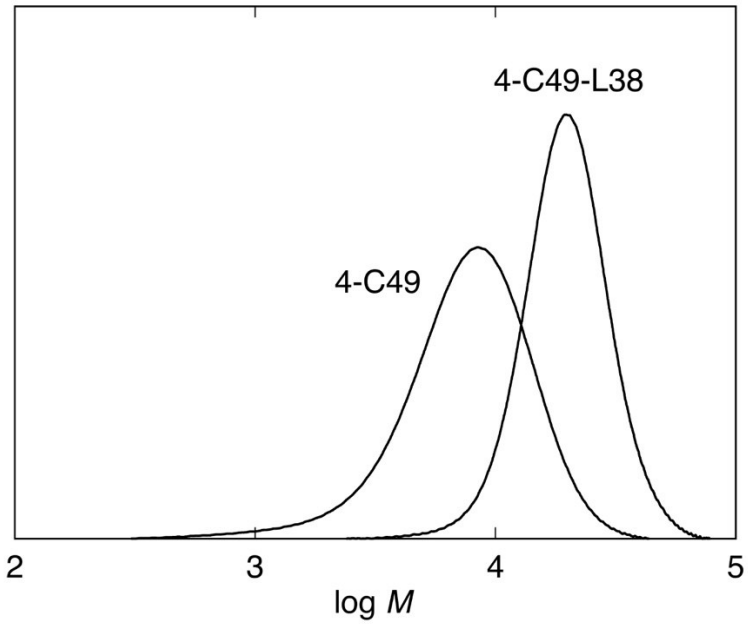

Figure S2. Typical GPC curves of 4-C and 4-C-L polymers (before and after 2nd step polymerization, 4-C49 and 4-C49-L38, respectively).

S3. Degree of crosslinking and crystallinity of samples (Table S1)

Code	DC[a] (%)	X_c(PCL)[b] (%)	X_c(PLLA)[b] (%)	X_c(tot)[c] (%)
4-L90		0.0	48.9	48.9
4-C28-L62		0.0	44.5	44.5
4-C49-L38		4.4	28.5	32.9
4-C49-L38 (SE) [d]		5.8	30.1	35.9
4-C69-L28		31.8	0.0	31.8
4-C93		58.5	0.0	58.5
4-L90/4-C93		35.1	1.6	36.7
N4-L90	99.6	0.0	0.0	0.0
N4-C28-L62	97.0	0.0	0.0	0.0
N4-C49-L38	93.9	0.0	0.0	0.0
N4-C69-L28	98.1	7.5	0.0	7.5
N4-C93	94.0	35.7	0.0	35.7
N4-L90/4-C93	73.6	13.4	0.0	13.4

Table S1. Crystallinity (X_c) of samples.

[a] Degree of crosslinking.
[b] X_c(PCL) and X_c(PLLA) are crystallinities of PCL and PLLA, respectively.
[c] $X_c(\text{tot}) = X_c(\text{PCL}) + X_c(\text{PLLA})$
[d] The sample was prepared by solvent evaporation, which is different from other copolymer samples prepared by precipitation but identical with the 4-L90/4-C93 blend sample.

S4. WAXD Profile of 4-C49-L38 sample prepared by solvent evaporation (Figure S3)

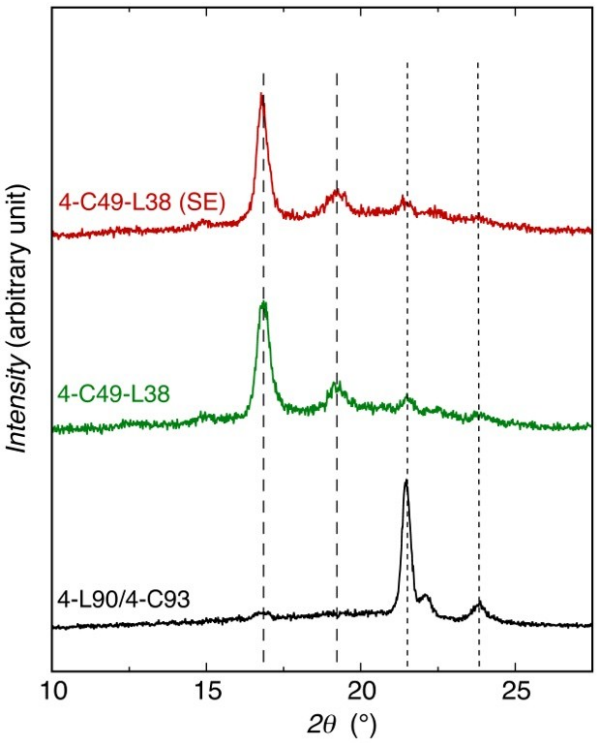

Figure S3. WAXD profile of 4-C49-L38 sample prepared by solvent evaporation (before crosslinking) [abbreviated as 4-C49-L38 (SE)], together with 4-C49-L38 sample prepared by precipitation and 4-L90/4-C93 blend sample prepared by solvent evaporation. The dashed and dotted lines indicate the main crystalline peak angles of PLLA α-(or δ-)form and PCL crystallites, respectively.

S5. Thermal properties of samples (Table S2)

Code	Heating								Cooling			
	T_g[a] (°C)	T_{cc}[a] (°C)	T_m(PCL)[a] (°C)	T_m(PLLA)[a] (°C)	ΔH_{cc}[b] (J g^{-1})	ΔH_m(PCL)[b] (J g^{-1})	ΔH_m(PLLA)[b] (J g^{-1})	ΔH(tot)[b] (J g^{-1})	T_c[d] (°C)	ΔH_c(PCL)[c] (J g^{-1})	ΔH_c(PLLA)[c] (J g^{-1})	ΔH_c(tot)[c] (J g^{-1})
4-L90	54.6	100.3		146.0	–0.5		32.6	32.0				
4-C28-L62				143.6			24.8	24.8	86.6		–18.9	–18.9
4-C49-L38			44.6	120.0		5.7	21.6	27.3	72.0		–16.1	–16.1
4-C49-L38 (SE)[d]			36.1, 43.5	119.3		5.7	20.4	26.1	70.5		–17.8	–17.8
4-C69-L28			22.4, 50.1			60.1		60.1	19.8	–41.7		–41.7
4-C93			61.6			90.0		90.0	34.2	–60.8		–60.8
4-L90/4-C93		99.6	54.8	132.7, 142.6	–5.4	56.0	14.9	65.5	32.6	–39.4		–39.4
N4-L90	60.7											
N4-C28-L62	32.2											
N4-C49-L38												
N4-C69-L28			24.7, 34.5			2.7		2.7				
N4-C93			47.4			46.5		46.5	19.1	–39.6		–39.6
N4-L90/4-C93	57.9		41.9	142.9	–1.9	29.7	2.6	30.4	9.6	–24.6		–24.6

Table S2. Thermal properties of samples.

[a] T_g, T_{cc}, and T_m(PCL), and T_m(PLLA) are glass transition and cold crystallization temperatures, and melting temperatures of PCL and PLLA, respectively.

[b] ΔH_{cc} and ΔH_m(PCL) and ΔH_m(PLLA) are enthalpies of cold crystallization and melting of PCL and PLLA, respectively. ΔH(tot) = ΔH_{cc}+ ΔH_m(PCL) + ΔH_m(PLLA).

[c] T_c, ΔH_c(PCL) and ΔH_c(PLLA) are crystallization temperature and crystallization enthalpies of PCL and PLLA, respectively. ΔH(tot) = ΔH_c(PCL) + ΔH_c(PLLA).

[d] The sample was prepared by solvent evaporation, which is different from other copolymer samples prepared by precipitation but identical with the 4-L90/4-C93 blend sample.

S6. DSC heating (a) and cooling (b) thermograms of 4-C49-L38 sample prepared by solvent evaporation (before crosslinking) (Figure S4)

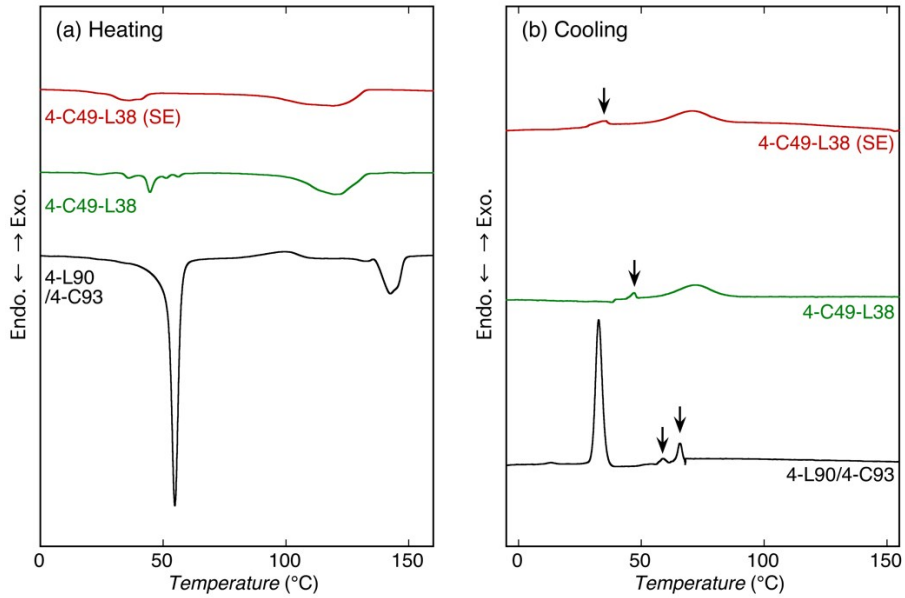

Figure S4. DSC heating (a) and cooling (b) thermograms of 4-C49-L38 sample prepared by solvent evaporation (before crosslinking) [abbreviated as 4-C49-L38 (SE)], together with 4-C49-L38 sample prepared by precipitation and 4-L90/4-C93 blend sample prepared by solvent evaporation. The exothermic peaks with arrows were formed due to replenishment of liquid nitrogen to the DSC apparatus.

S7. Enthalpies of cold crystallization and melting of samples before and after crosslinking for heating scanning (Figure S5)

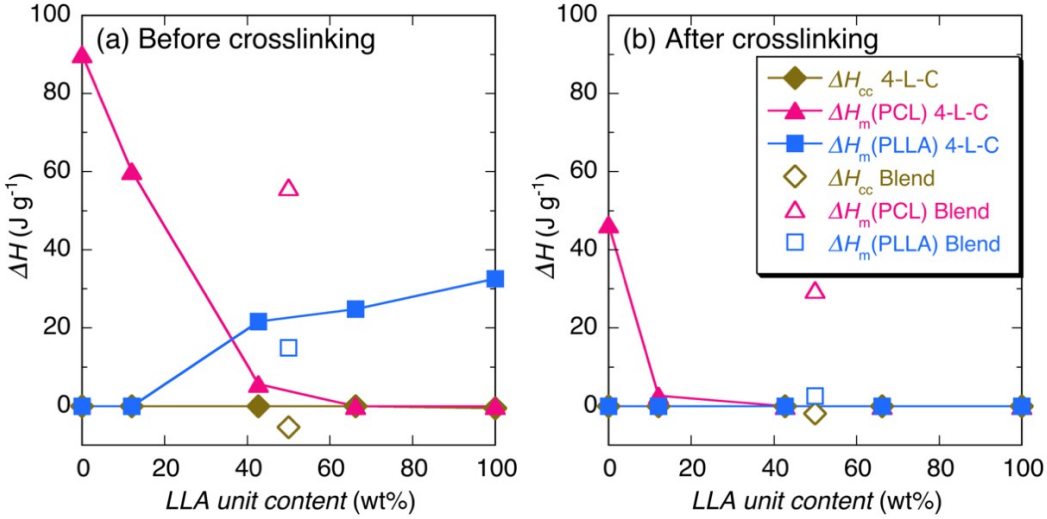

Figure S5. Enthalpies of cold crystallization and melting of samples before (a) and after (b) crosslinking for heating scanning.

S8. Enthalpies of crystallization of samples before and after crosslinking for cooling scanning (Figure S6)

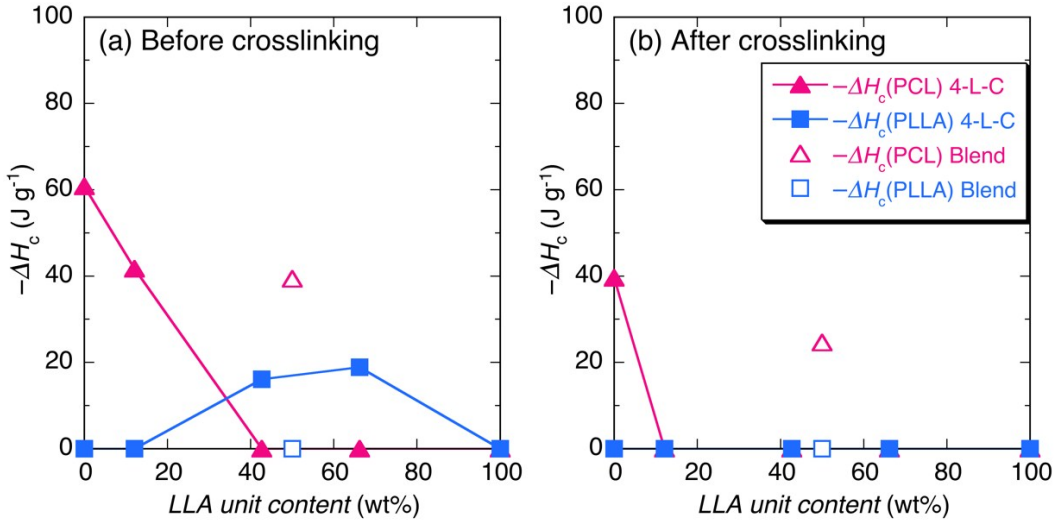

Figure S6. Enthalpies of crystallization and melting of samples before (a) and after (b) crosslinking for cooling scanning.

S9. Relative crystallinity (X_r) of samples before and after crosslinking for cooling scanning (Figure S7)

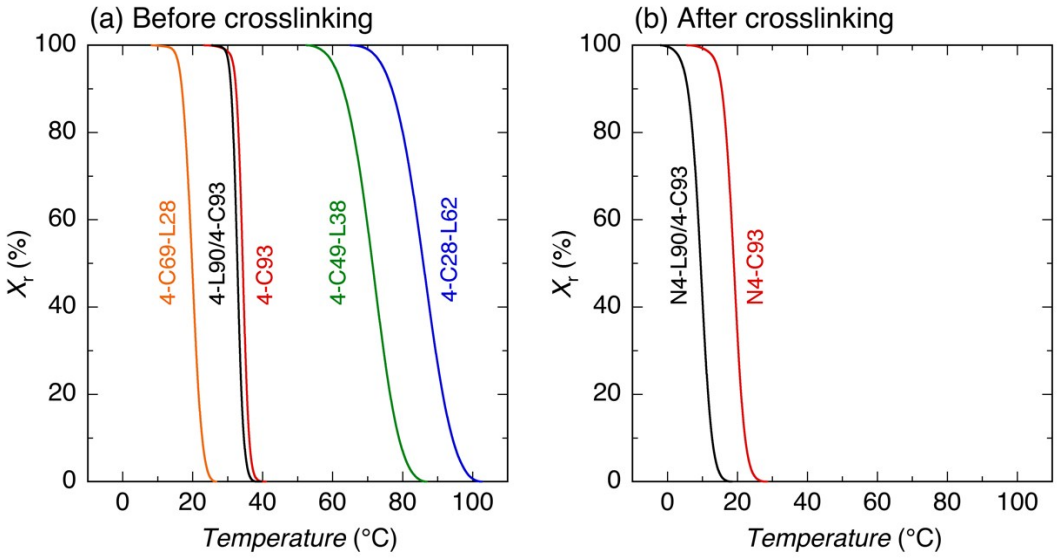

Figure S7. Relative crystallinity (X_r) of samples before (a) and after (b) crosslinking for cooling scanning as a function of temperature.