Electronic Supporting Information (ESI) for

Thermoset Elastomers Covalently Crosslinked by Hard Nanodomains of Triblock Copolymers Derived from Carvomenthide and Lactide: Tunable Strength and Hydrolytic Degradability†

Jeongmin Jang,‡[a, b] Hyejin Park,‡[a, b] Haemin Jeong,[a, c] Eunbi Mo,[a, b] Yongbin Kim,[a, b] Jeong Suk Yuk,[a] Siyoung Q. Choi,[d] Young-Wun Kim,[a, c] and Jihoon Shin*[a, c]

[a]Center for Environment & Sustainable Resources, Korea Research Institute of Chemical Technology (KRICT), 141 Gajeong-ro, Yuseong-gu, Daejeon, 34114, Korea. E-mail: jshin@krict.re.kr

[b]Department of Chemical Engineering, Inha University, 100 Inharo, Nam-gu, Incheon, 22212, Korea.

[c]Department of Advanced Materials & Chemical Engineering, University of Science & Technology (UST), 217 Gajeong-ro, Daejeon, 34113, Korea.

[d]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, Korea.

†Electronic supplementary information (ESI) available: Experimental, NMR, DSC, TGA, SAXS, Tensile data. See DOI:

‡These authors contributed equally to this work.

Supporting Information consists of five figures over twelve pages.

Contents of Supporting Information

(−PCM6−PLA4−COOH)$_2$, (−PCM7−PLA3−COOH)$_2$, and (−PCM8−PLA2−COOH)$_2$, and (d) the purified (−PCM6−PLA4−COOH)$_2$, (−PCM7−PLA3−COOH)$_2$, and (−PCM8−PLA2−COOH)$_2$ ((a), (b), (c): before purification) (* = PCM homopolymer and ** = 1,4-dioxane).

Annexure S1

Materials

All air or/and moisture sensitive reagents were handled in a nitrogen charged glovebox. Diethylene glycol (DEG) (≥99.0%, Sigma-Aldrich, St. Louis, MO) used for polymerizations was purified under reduced pressure over sodium and stored in the glovebox. Tin(II) 2-ethylhexanoate (92.5−100.0%, Sigma-Aldrich, St. Louis, MO) used for polymerization was also distilled (3×) and stored in the glovebox. D,L-lactide (LA) (>99.5%, Corbion Purac, Amsterdam, Netherland) were recrystallized twice with toluene prior to being stored in a glove box. D-Dihydrocarvone (mixture of isomers, natural, 97%), palladium on carbon (10 wt % loading, matrix activated carbon support), OXONE® (monopersulfate compound, $KHSO_5$ • $^1/_2KHSO_4$ • $^1/_2K_2HSO_4$), and succinic anhydride (≥99%) were used as received from Sigma-Aldrich (St. Louis, MO) without further purification. Trimethylolpropane tris(2-methyl-1-aziridinepropionate) (TAz) purchased from Tokyo Chemical Industry (TCI, Tokyo, Japan) for crosslinking was used as received without purification. Trimethylolpropane tris(2-methyl-1-aziridinepropionate) (TAz) purchased from Tokyo Chemical Industry used for crosslinking was used as received without purification. Chloroform and methanol (HPLC grade, Burdick & Jackson, Morristown, NJ) for polymer precipitation were also used as received without further purification. Glass pressure vessels, Teflon caps, and Teflon-coated magnetic stir bars were fully dried at 130 °C before using in the glovebox.

Synthesis of Carvomenthide (CM)

CM was obtained from D-dihydrocarvone using a literature procedure. D-Dihydrocarvone (100.0 g; 657 mmol), palladium on carbon (10 wt % and 1 g; 0.94 mmol) as a catalyst, and *n*-hexane (300mL) as a solvent were added into a high-pressure reactor (Parr Instrument Company, Moline, IL). The reactor was sealed and purged three times with 15 bar of nitrogen to remove the inner air. The solution was then

charged with 15 bar of hydrogen and reacted at room temperature with rapid stirring. The reactor was recharged with hydrogen once again when the pressure deceased to about 5 bar. The additional reaction was allowed to proceed with overnight before dismantling the reactor. ^{1}H NMR (700 MHz, CDCl$_3$): δ 2.48−2.27 (m, 2H major, 3H minor), 2.12−2.02 (m, 2H major), 1.91−1.82 (m, 1H major, 1H minor), 1.75−1.38 (m, 3H major, 5H minor), 1.35−1.25 (m, 1H major), 1.09 (d, J = 7.0 Hz, 3H minor), 1.01 (d, J = 6.5 Hz, 3H major), 0.89 (m, 6H major, 6H minor). ^{13}C NMR (125 MHz, CDCl$_3$): δ 212.8, 46.2, 44.9, 44.4, 34.7, 32.3, 28.5, 19.2, 18.9, 13.9 (major isomer); 214.2, 44.3, 43.8, 42.6, 30.9, 30.1, 24.6, 19.6, 19.5, 15.4 (minor isomer). The following as a green procedure was performed for the preparation of CM using OXONE$^®$ in an aqueous ethanol solution. A round-bottomed flask (1 L) was charged with D-carvomenthone (6.850 g, 44.4 mmol), sodium bicarbonate (29.9g, 355 mmol), and ethanol absolute (200 proof, 200 mL). The reaction was stirred at room temperature when a solution of OXONE$^®$ (54.6 g, 177.6 mmol) in water (200 mL) was dropwised using a syringe pump over 48 h. After the addition was stopped, the reaction was allowed to stir for an addition 8 h. The reaction mixture was vacuum-filtered through Celite 545 to remove any remaining solid. The filtrate was concentrated to about 10 mL via rotary evaporation under reduced pressure, affording the conversion of ~99%, as determined by ^{1}H NMR analysis. The product was purified by three time vacuum distillation (90−100 °C, 120 mTorr) to give CM, which was a colorless and transparent oil (4.19g, 24.6 mmol and overall yield of 56%). ^{1}H NMR (700 MHz, CDCl$_3$): δ 4.42 (qdd, J = 9.6, 6.4, and 9.4 Hz, 1H major, 1H minor), 2.80 (dd, J = 5.7 and 14.1 Hz, 1H minor), 2.75 (dd, J = 3.7 and 14.1 Hz, 1H minor), 2.47 (m, 2H major), 1.91 (td, J = 3.8 and 15.2 Hz, 1H major, 1H minor), 1.81 (d, J = 13.3 Hz, 1H major, 1H minor), 1.73−1.40 (m, 4H major, 4H minor), 1.34 (dd, J = 6.4 and 1.6 Hz, 3H major, 3H minor), 1.03−0.88 (dd, J = 6.4 and 60.4 Hz, 6H minor), 0.91−0.85 (dd, J = 6.9 and 11.5 Hz, 6H major). ^{13}C NMR (125 MHz, CDCl$_3$): δ 174.7, 75.7, 39.7, 37.3, 35.2, 32.8, 30.5, 21.9, 18.1, 17.8 (major isomer); 173.3, 75.5, 38.1, 37.7, 31.5, 29.3, 28.3, 21.6, 20.0, 19.4 (minor isomer).

One-Pot, Three-Step Process for Synthesis of Carboxy-Telechelic Poly(Lactide)−Poly(Carvomenthide)−Poly(Lactide) (−PCM−PLA−COOH)₂

(a) Synthesis of Hydroxyl-Telechelic Poly(Carvomenthide) (−PCM−OH)₂. The hydroxyl-terminated poly(carvomenthide) was synthesized by bulk ring-opening polymerization (ROP) of carvomenthide (CM). In a nitrogen-filled glovebox, DEG (1 equiv), Sn(Oct)₂ (0.1 equiv), and CM (60, 71, 83 or 95 equiv to target the molar masses of 10, 12, 14 and 16 kg mol⁻¹) were transferred to a pressure vessel (350 mL) with a magnetic bar. The sealed reaction vessel was taken out of the glovebox and placed in a thermoset oil bath at 100 °C for 25 h (ca. 95−97% conversion of CM and 70−80% isolated yield based the product weigh calculated by the conversion, after precipitation for purification). ¹H NMR (700 MHz, CDCl₃): δ 4.86 (m, 1H, H$_d$ from the repeating unit of PCM), 4.22 (m, 2H, H$_b$ from incorporated initiator), 3.78 (m, 1H, H$_a$ from the end unit of hydroxyl PCM), 3.69 (t, J = 4.9 Hz, 2H, H$_c$ from incorporated initiator), 2.25 (dd, J = 5.4 and 15.1 Hz, 1H from the repeating unit of PCM), 2.10 (dd, J = 7.2 and 15.1 Hz, 1H from the repeating unit of PCM), 1.73 (m, 2H from the repeating unit of PCM), 1.58 (m, 1H from the repeating unit of PCM), 1.47 (m, 1H from the repeating unit of PCM), 1.32 (m, 1H from the repeating unit of PCM), 1.24 (m, 1H from the repeating unit of PCM), 1.19 (d, J = 6.1 Hz, 3H from the repeating unit of PCM), 0.85 (dd, J = 6.7 and 12.9 Hz, 6H from the repeating unit of PCM). ¹³C NMR (125 MHz, CDCl₃): δ 173.5, 173.3, 71.1, 70.9, 69.0 (DEG), 67.8, 63.2 (DEG), 40.5, 36.3, 33.4, 29.7, 26.6, 19.9, 19.1, 18.6.

(b) Synthesis of Hydroxyl-Terminated Pol(Lactide)−Poly(Carvomenthide)−Poly(Lactie) (−PCM−PLA−OH)₂. The hydroxyl-ended (−PCM−PLA−OH)₂ was also prepared by bulk ring-opening transesterification polymerization (ROTEP) of D,L-lactide (LA) with (−PCM−PLA−OH)₂ as a macroinitiator. After the vessel was cooled to room temperature, it was transferred to the glovebox. LA (74, 61, 47 and 32 equiv to target molar masses of 10, 8, 6 and 4 kg mol⁻¹ as PLA hard domains in the triblocks) was added into the reaction vessel without any additional amount of Sn(Oct)₂. The vessel was

resealed and placed in a thermoset oil bath at 110 °C for 3−7 h (ca. 95−98% conversion of LA and 80−90% isolated yield based the product weigh calculated by the conversion, after precipitation for purification). ^{1}H NMR (700 MHz, CDCl$_3$): δ 5.25−5.12 (m, 1H, H$_f$ from the repeating unit of PLA), 4.86(m, 1H, H$_d$ from the repeating unit of PCM), 4.36 (m, 1H, H$_e$ from the end unit of PLA), 4.22 (m, 2H, H$_b$ from incorporated initiator), 3.69 (t, J = 4.9 Hz, 2H, H$_c$ from incorporated initiator), 2.25(dd, J = 5.4 and 15.1 Hz, 1H from the repeating unit of PCM), 2.10 (dd, J = 7.2 and 15.1 Hz, 1H from the repeating unit of PCM), 1.73 (m, 2H from the repeating unit of PCM), 1.60-1.53 (m, 1H from the repeating unit of PCM and 3H from the repeating unit of PLA), 1.47 (m, 1H from the repeating unit of PCM), 1.32 (m, 1H from the repeating unit of PCM), 1.24 (m, 1H from the repeating unit of PCM), 1.19 (d, J = 6.1 Hz, 3H from the repeating unit of PCM), 0.85 (dd, J = 6.7 and 12.9 Hz, 6H from the repeating unit of PCM). ^{13}C NMR (125 MHz, CDCl$_3$): δ 173.5, 173.3, 169.6−169.1 (PLA), 71.1, 70.9, 69.2 (PLA), 69.0 (DEG), 63.2 (DEG), 40.5, 36.3, 33.4, 29.7, 26.6, 19.9, 19.1, 18.6, 16.8−16.5 (PLA).

(c) Synthesis of Carboxy-Telechelic Pol(Lactide)−Poly(Carvomenthide)−Poly(Lactie) (−PCM−PLA−COOH)$_2$. The general procedure to prepare the carboxy-telechelic triblock via post-polymerization functionalization was as follows: 1,4-Dioxane and (−PCM−PLA−OH)$_2$ was added to the vessel and the mixture was stirred to dissolve the polymer at room temperature for 30 min. An excess of succinic anhydride (SA) (36 equiv for one hydroxyl group (1 equiv) in (−PCM−PLA−OH)$_2$) and dimethylaminopyridine (DMAP) (0.01 equiv) as a catalyst were added into the reaction vessel. The sealed vessel was placed in a thermostatic oil bath at 90 °C for 50 h. After cooling the vessel, the reaction was quenched by adding chloroform to precipitate most of unreacted SA. The solution was vacuum-filtered through Celite 545 to remove the precipitated SA solid. The filtrate was precipitated into cold methanol to dissolve SA and recover the polymers, which were dried at 80 °C (>99% conversion from hydroxyl group to carboxy group and 60−70% isolated yield base on the product weight calculated by the conversion). ^{1}H NMR (700 MHz, CDCl$_3$): δ 5.25−5.12 (m, 1H, H$_f$ from the

repeating unit of PLA), 4.86(m, 1H, H_d from the repeating unit of PCM), 4.22 (m, 2H, H_b from incorporated initiator), 3.69 (t, $J = 4.9$ Hz, 2H, H_c from incorporated initiator), 2.71 (dd, $J = 6.0$ and 24.2 Hz, 4H, H_j from the end unit of carboxy-terminated triblock), 2.25(dd, $J = 5.4$ and 15.1 Hz, 1H from the repeating unit of PCM), 2.10 (dd, $J = 7.2$ and 15.1 Hz, 1H from the repeating unit of PCM), 1.73 (m, 2H from the repeating unit of PCM), 1.60−1.53 (m, 1H from the repeating unit of PCM and 3H from the repeating unit of PLA), 1.47 (m, 1H from the repeating unit of PCM), 1.32 (m, 1H from the repeating unit of PCM), 1.24 (m, 1H from the repeating unit of PCM), 1.19 (d, J = 6.1 Hz, 3H from the repeating unit of PCM), 0.85 (dd, $J = 6.7$ and 12.9 Hz, 6H from the repeating unit of PCM).

Characterization

The ^{1}H and ^{13}C NMR spectra of the polymeric compounds dissolved in CDCl$_3$ were obtained using a Bruker Avance III HD-700 spectrometer (700 MHz) and Bruker DPX-500 spectrometer (125 MHz), respectively. Tetramethylsilane (TMS) was used as the internal standard.

Size exclusion chromatography (SEC) for the prepared polymers was done on an Agilent 1260 Infinity LC system equipped with a refractive index detector. The samples were diluted in tetrahydrofuran (mobile phase) and passed through one PLgel guard column (5 μm, 7.5 × 50 mm) and three PLgel Mixed-C columns (5 μm, 7.5 × 300 mm) at 35 °C under a constant flow rate of 1 mL min^{-1}. The M_n and M_w values were calculated with the calibration curve which was fitted with polystyrene standards.

Differential scanning calorimetry (DSC) analysis was performed on TA Q-1000 DSC under a nitrogen atmosphere. The polymer samples (5–10 mg) were loaded into hermetically sealed aluminum DSC and heated to 130 °C and held for 5 min; then, they were allowed to cool to −80 °C and held there for 1 min. The samples were reheated to 130 °C. The rates of heating and cooling were 10 °C min^{-1}. The transition and melting temperatures were obtained during the second heating step. Thermal gravimetric

analysis (TGA) was performed by TA Q-500 TGA under a nitrogen atmosphere at heating rate of 10 °C min^{-1} in a temperature range from 25 to 430 °C.

Thin film surface morphology was investigated by tapping mode AFM (Atomic Force Microscopy, Multimode 8® Nanoscope system, Bruker). In an attempt to visualize this effect on AFM, the films for the thermoplastic triblocks were prepared by spin-coating (3000 rpm) of the polymer solutions (5 wt/vol %) using methylene chloride on silicon wafer substrates (1 × 1 cm) which was used without any cleaning. For the films having the thermoset triblock, the solution of the carboxy-telechelic precursors and the aziridine crosslinker were spin-coated, which was cured at high temperature (180 °C) for 5 min. The thickness of the AFM film layers for the block copolymers was ranged 200 to 300 nm.

Synchrotron-based small-angle X-ray scattering (SAXS) measurement was taken at Pohang Accelerator Laboratory (Pohang, Korea). The SAXS data at high temperature (60 °C) and room temperature were recorded with a monochromatized X-ray radiation source of 11.11 KeV (0.1116 nm) with the sample-to-detector distance of 4.514 m or 11.54 keV (0.1074 nm) with 2048 × 2048 pixels. The two-dimensional scattering patterns were azimuthally integrated to afford one-dimensional profiles presented as scattering vector (q) versus scattered intensity, where the magnitude of scattering vector is given by $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle.

Dynamic Mechanical Analysis (DMA) was carried out using an ARES-G2 rotational rheometer (Waters) under nitrogen condition. The storage and loss moduli as functions of temperature from −80 to 160 °C were collected at a heating rate of 3 °C min^{-1} and a frequency of 1 Hz.

Uniaxial tensile testing for normal strain-stress of the prepared samples were conducted out using a universal testing machine (QRS-S11H, Quro) at room temperature. Polymer films with thickness of 0.3−0.4 mm were prepared by solvent casting method using chloroform. After evaporating the solvent at room temperature for 3 days, the samples were further dried at 70 °C for 12 h under vacuum. For all samples, dog-bone microtensile bars were made from the films using a punch press with the following

dimension described by ASTM D1708. Specimens were drawn until failure with a constant rate of 130 mm min^{-1} with 100 N load cell; all values are reported as the average and standard deviation of at least four samples.
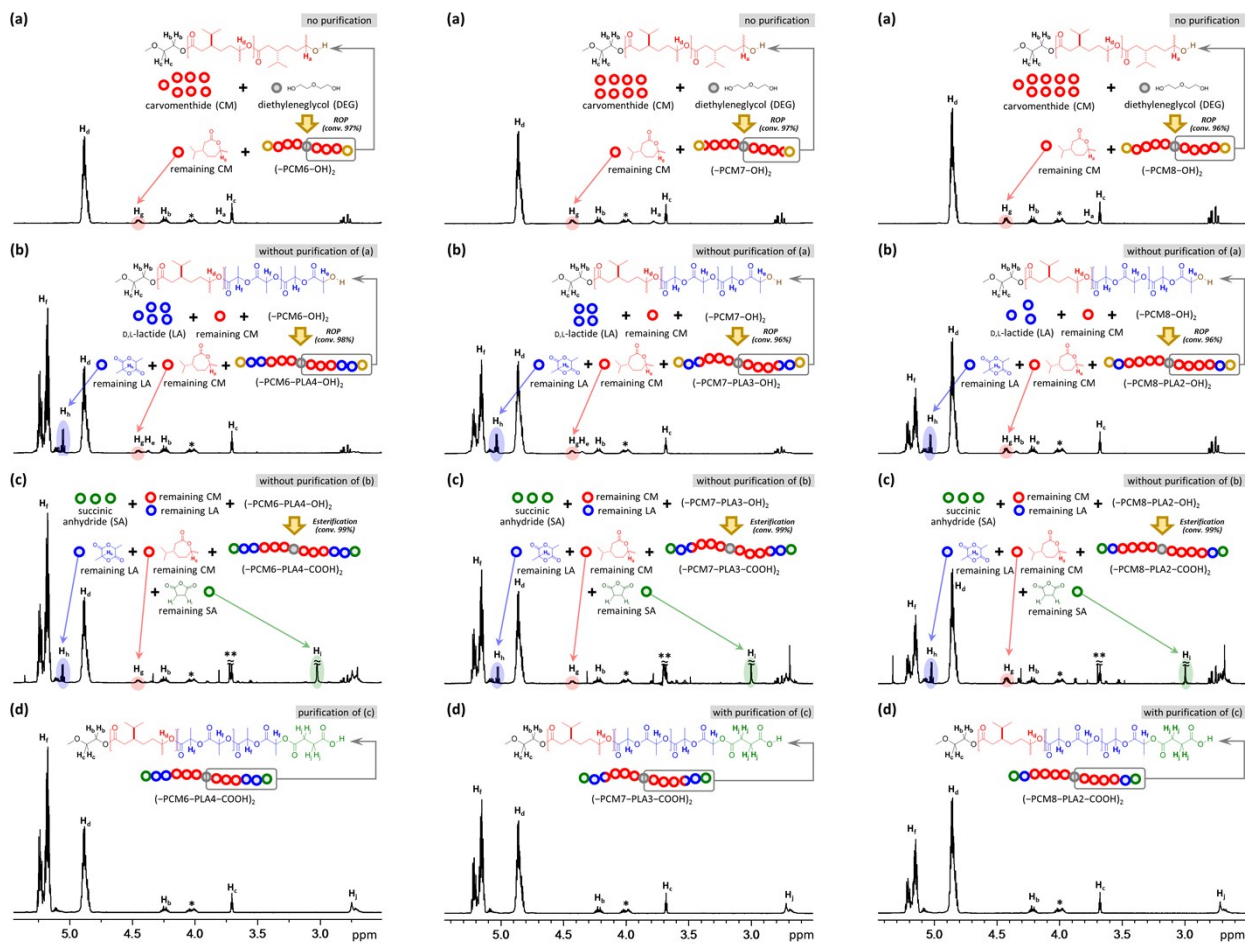
Fig. S1 ^{1}H NMR spectra of (a) (−PCM6−OH)$_2$, (−PCM7−OH)$_2$, and (−PCM8−OH)$_2$ (b) (−PCM6−PLA4−OH)$_2$, (−PCM7−PLA3−OH)$_2$, and (−PCM8−PLA2−OH)$_2$ (c) (−PCM6−PLA4−COOH)$_2$, (−PCM7−PLA3−COOH)$_2$, and (−PCM8−PLA2−COOH)$_2$, and (d) the purified (−PCM6−PLA4−COOH)$_2$, (−PCM7−PLA3−COOH)$_2$, and (−PCM8−PLA2−COOH)$_2$ ((a), (b), (c): before purification) (* = PCM homopolymer and ** = 1,4-dioxane).
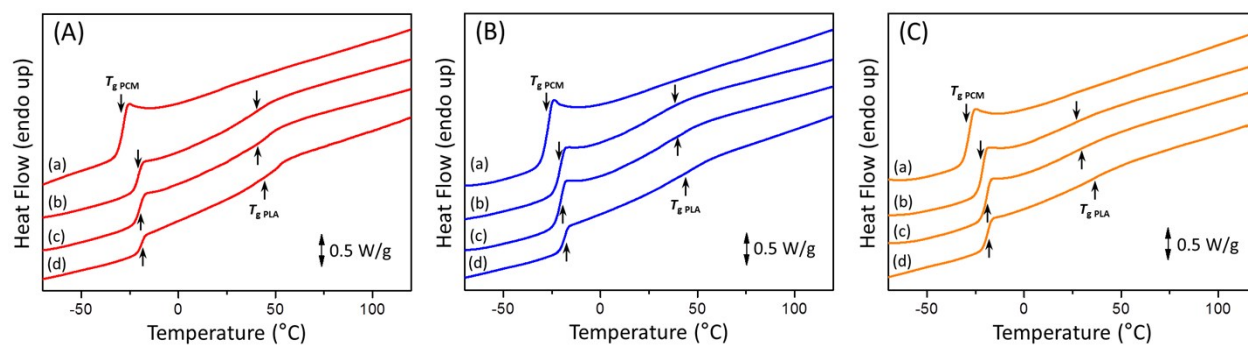
Fig. S2 DSC traces of (A-a) (−PCM6−OH)$_2$, (A-b) (−PCM6−PLA4−OH)$_2$, (A-c) (−PCM6−PLA4−COOH)$_2$, (A-d) XL−(PLA4−PCM12−PLA4), (B-a) (−PCM7−OH)$_2$, (B-b) (−PCM7−PLA3−OH)$_2$, (B-c) (−PCM7−PLA3−COOH)$_2$, (B-d) XL−(PLA3−PCM14−PLA3), (C-a) (−PCM8−OH)$_2$, (C-b) (−PCM8−PLA2−OH)$_2$, (C-c) (−PCM8−PLA2−COOH)$_2$, and (C-d) XL−(PLA2−PCM16−PLA2). Arrows indicate glass transition temperatures ($T_{g\ PCM}$ and $T_{g\ PLA}$) for rubbery PCM-rich phases and hard PLA-rich microdomains.
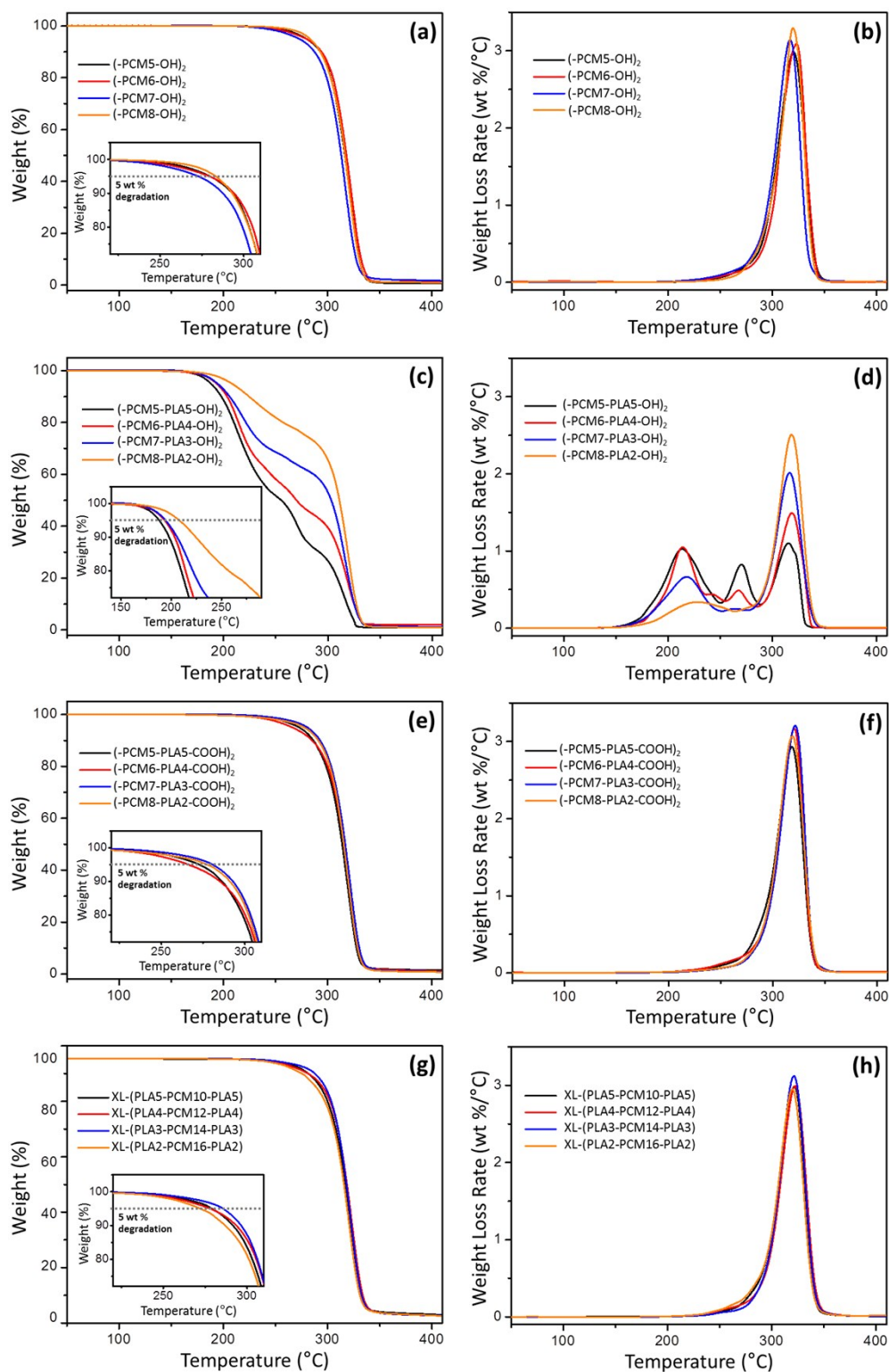
Fig. S3 TGA weight loss and DTG curves for $(-PCM-OH)_2$, $(-PCM-PLA-OH)_2$, $(-PCM-PLA-COOH)_2$, and $XL-(PLA-PCM-PLA)$.
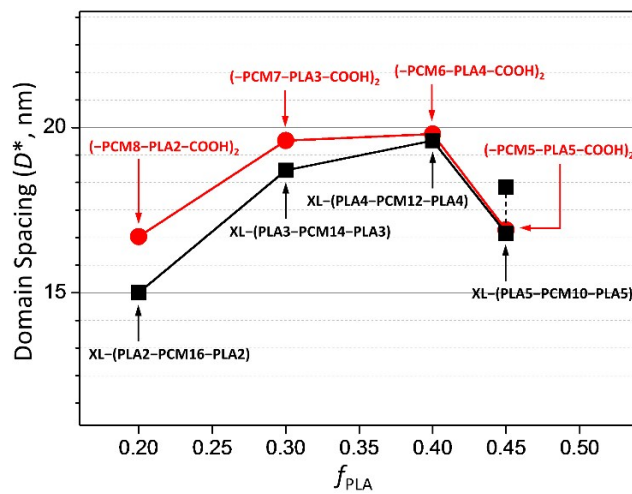
Fig. S4 The domain spacing (*D**) values calculated by SAXS profiles *vs* f_{PLA} in the uncured (−PCM−PLA−COOH)$_2$ vs the cured XL−(PLA−PCM−PLA) samples.
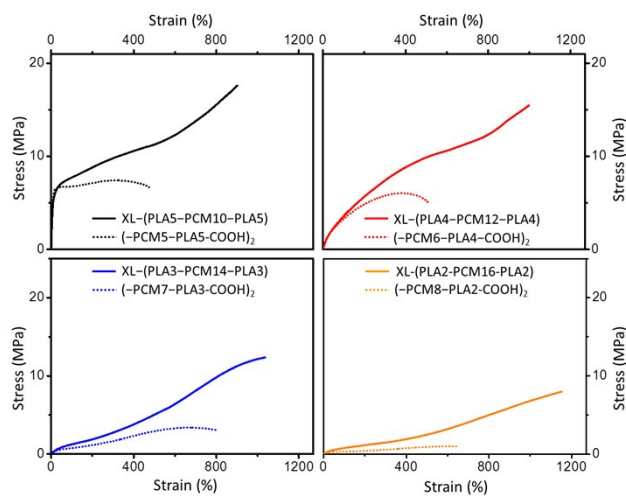
Fig. S5 Comparison of stress-strain curves of the (−PCM−PLA−COOH)$_2$ thermoplastic copolymers and the XL−(PLA−PCM−PLA) thermoset elastomers.