

Supporting Information

New Transparent Poly(L-lactide acid) Films as High-Performance Bio-Based Nanocomposites

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Experimental Section

Materials

All commercially-available chemicals and reagents were of the highest purity or grade and were obtained from Sigma-Aldrich (St. Louis, MO, USA). All solvents were high-performance liquid chromatography (HPLC) grade and purchased from TEDIA (Fairfield, OH, USA). Toluene and tetrahydrofuran (THF) were distilled over calcium hydride prior to use. Poly(L-lactic acid) (PLLA) was purchased from Weimon Inc. (Taipei City, Taiwan). Gel permeation chromatography (GPC) analysis indicated that the molecular weight of PLLA was ca. 172,711 g/mol, with a polydispersity index (PDI; M_w/M_n) of 1.58. PLLA has a melting point of 158-174 °C and glass transition temperature of around 60 °C.

Measurements

Nuclear magnetic resonance (NMR). ^1H -NMR and ^{13}C -NMR spectra were recorded using a Varian Inova-400 MHz spectrometer equipped with a magnetic field strength of 9.395 T. The samples (15 mg each) were dissolved in 0.5 ml of the deuterated solvent in a 5 mm NMR tube. All NMR experiments were carried out at 25 °C.

Gel permeation chromatography (GPC). Weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index (PDI; M_w/M_n) were measured using a Waters 410 GPC system equipped with a refractive index detector and three Ultrastyrigel™ columns (100, 500 and 1000 Å) connected in series. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 ml/min at 40 °C. The system was calibrated using polystyrene (PS) standards (Polymer Standards Service, Silver Spring, MD, USA).

Wide-Angle X-ray Diffraction (WAXD). Prior to the WAXD experiments, all samples were annealed at 180 °C for 20 min and slowly cooled down to the room temperature at a rate less than 3 °C/min. WAXD spectra of the powders were obtained at room temperature using a Rigaku D/max-2500 X-ray diffractometer with Ni-filtered Cu K α radiation, operated at 30 kV and 200 mA. Radiation with a wavelength of 0.154 nm was used. All test samples were mounted on a threaded circular sample holder; the data were collected using a proportional counter detector over the 2θ range from 2 to 40° scanning at a rate of 2° min $^{-1}$.

Differential Scanning Calorimetry (DSC). A DSC instrument (TA Instruments Q-20, New Castle, DE, USA) was used to perform thermal measurements at a heating and cooling rate of 10 °C/min. Test samples of 4–6 mg in aluminum pans were analyzed over the temperature range of 25–200 °C. The second heating scans are presented in Figure 3, and the measured T_m and ΔH are summarized in Table S1.

Ultraviolet-Visible (UV-Vis) spectroscopy. UV-Vis spectroscopy was performed using a HP 8453 diode-array spectrophotometer (Hewlett-Packard, Waldbronn, Germany). The optical transmittance of each film was

assessed at 600 nm.

Tensile Tests. Tensile tests were performed using a universal testing machine (EZ-L; Shimadzu Corp, Kyoto, Japan) at ambient conditions (25 °C, 65% relative humidity) under a constant cross-head speed of 10.0 mm/min.

Dynamic Mechanical Analysis (DMA). DMA measurements were performed using a DSC DMA800 (TA Instruments Inc., New Castle, PA, USA), under the following conditions: frequency, 1 Hz; tensile preload, 0.01 N; and strain amplitude, 30 μm . Each sample was heated from 0 °C to 120 °C at a rate of 3 °C/min in an atmosphere of nitrogen gas.

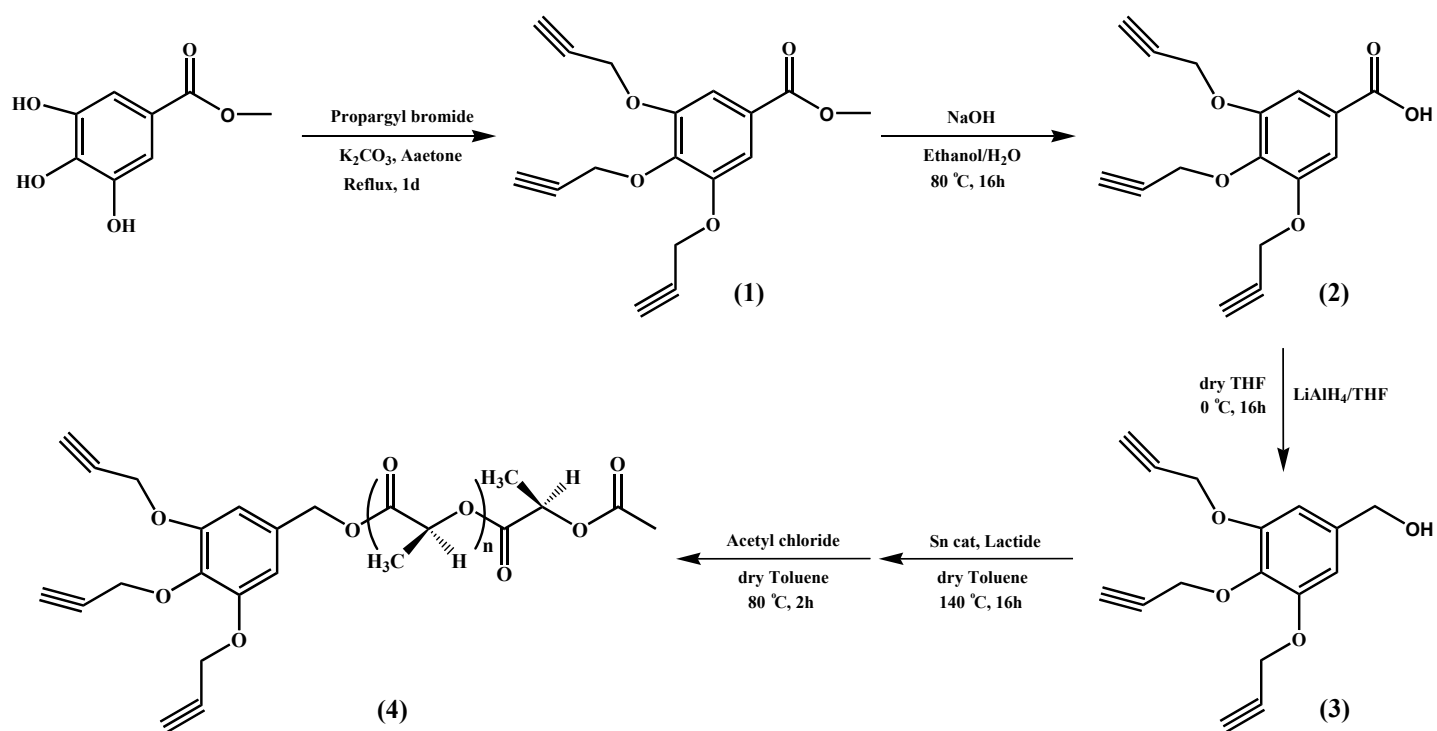
Scanning Electron Microscopy (SEM). The films were fractured under liquid nitrogen, and then the fractured surface was firmly adhered onto the silicon substrate, sputtered with gold and visualized using a field emission SEM (Hitachi S-4700, Tokyo, Japan) at an accelerating voltage of 10 kV.

Transmission Electron Microscopy (TEM). TEM images of ultra-thin sections of the polymer films placed on carbon-coated copper grids were recorded using an FEI T12 transmission electron microscope (FEI Co., Eindhoven, Netherlands) with a low-energy electron beam (120 keV).

Gas Permeability. Gas permeability tests were performed in oxygen at 23 °C on an OX-TRAN 2/21 unit (Mocon Inc., Minneapolis, MN, USA), in accordance with American Society for Testing and Materials (ASTM) D3985. The samples were prepared in pieces with an area of 50 cm² and a film thickness of approximately 0.45 mm using the hot press method at a pressure of 7 Bar and temperature of 190 °C.

Biodegradable Experiments. Hydrolytic degradation of all samples was assessed in neutral water (pH 7.0) at 25 °C and 55% relative humidity. The degradation rate of each film was assessed by GPC to determine the reduction in molecular weight during the degradation period.

Syntheses



Scheme S1. Synthetic procedures for Tripropargyl-PLLA.

Synthesis of methyl 3,4,5-tris(prop-2-ynoxy)benzoate (1)

Methyl 3,4,5-trihydroxybenzoate (10 g, 0.054 mol) and anhydrous potassium carbonate (24.0 g, 0.173 mol) were dissolved into 150 ml of acetone in a flask, then 1,10-dibromodecane (45.68 ml, 0.203 mol) was added and the reaction mixture was stirred at 70 °C for 1 d. The crude oil sample was collected by first by filtration then the solvent was removed using a rotary evaporator. The insoluble materials were removed by suction filtration using a Büchner funnel, remaining solvent was removed on a rotary evaporator and the product was recrystallized twice from petroleum ether. Yield: 95% (15.3 g).

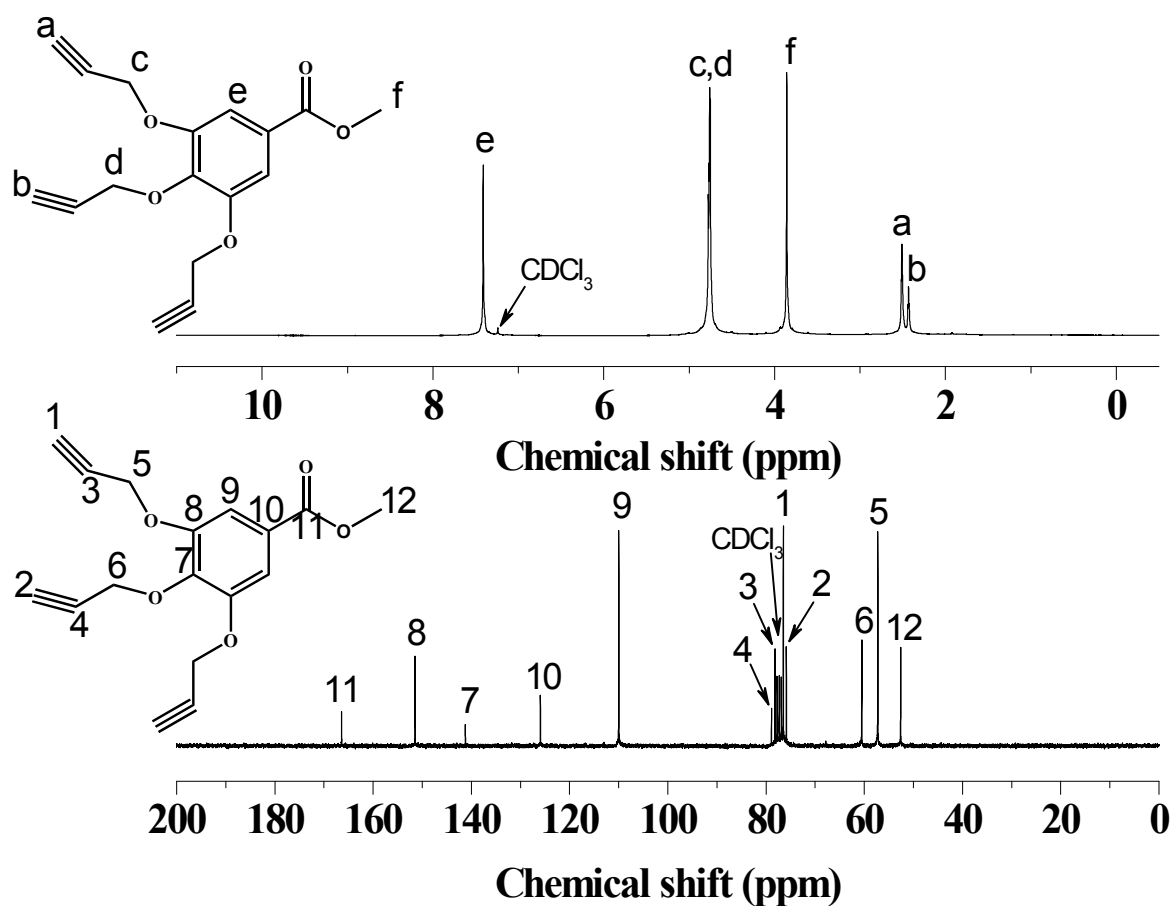


Figure S1. ^1H NMR and ^{13}C NMR spectra of compound (1) in CDCl_3 .

Synthesis of 3,4,5-tris(prop-2-ynyloxy)benzoic acid (2)

Potassium hydroxide (1.68 g, 30 mmol) was added to a solution of (1) (10 g, 0.034 mol) in a mixed solvent of ethanol (65 ml) and water (10 ml). After 16 h of reflux, the reaction mixture was cooled to room temperature and poured into water (1000 ml). While stirring, 1 M hydrochloric acid was slowly added to the mixture until the mixture reached pH 1. The white product was isolated by filtration and used for the next reaction without further purification. Yield: 97 % (9.3 g).

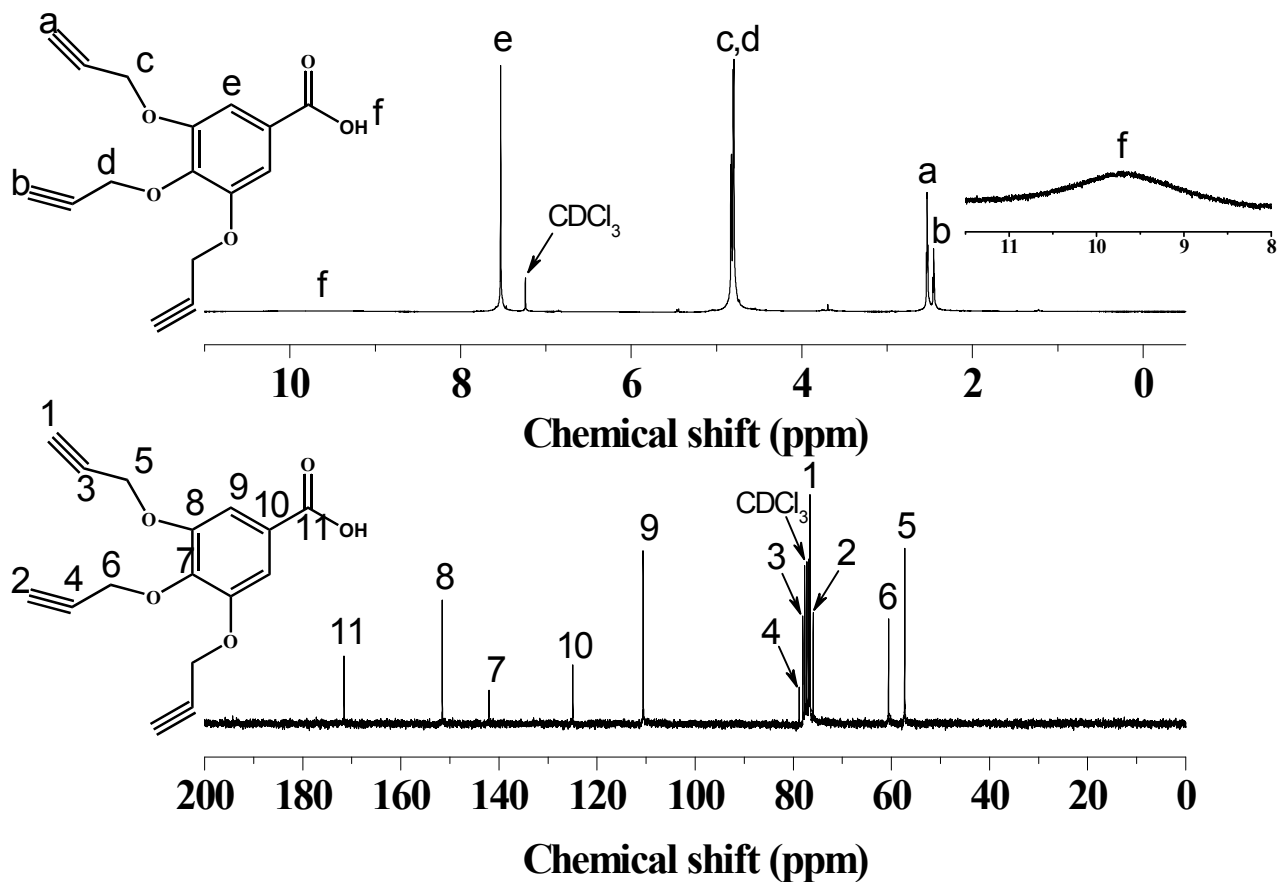


Figure S2. ¹H NMR and ¹³C NMR spectra of compound (2) in CDCl₃.

Synthesis of (3,4,5-tris(prop-2-ynyloxy)phenyl)methanol (3)

A solution of (2) (10 g, 0.035 mol) in anhydrous THF (150 ml) was added dropwise to a suspension of lithium aluminum hydride (LiAlH₄) in anhydrous THF (22.5 ml, 0.045 mol, 2.0 M in THF) at 0 °C with stirring in a nitrogen gas atmosphere. The reaction mixture was stirred at 0 °C for 1 h, then maintained at room temperature for an additional 10 h. Subsequently, the reaction was quenched with water (100 ml), the resulting solution was extracted with dichloromethane (3 × 50 mL) and the combined organic layers were dried over magnesium sulfate and filtered. After filtration, the solvent was removed under reduced pressure to yield the final product, a white powder. Yield: 70 % (6.7 g).

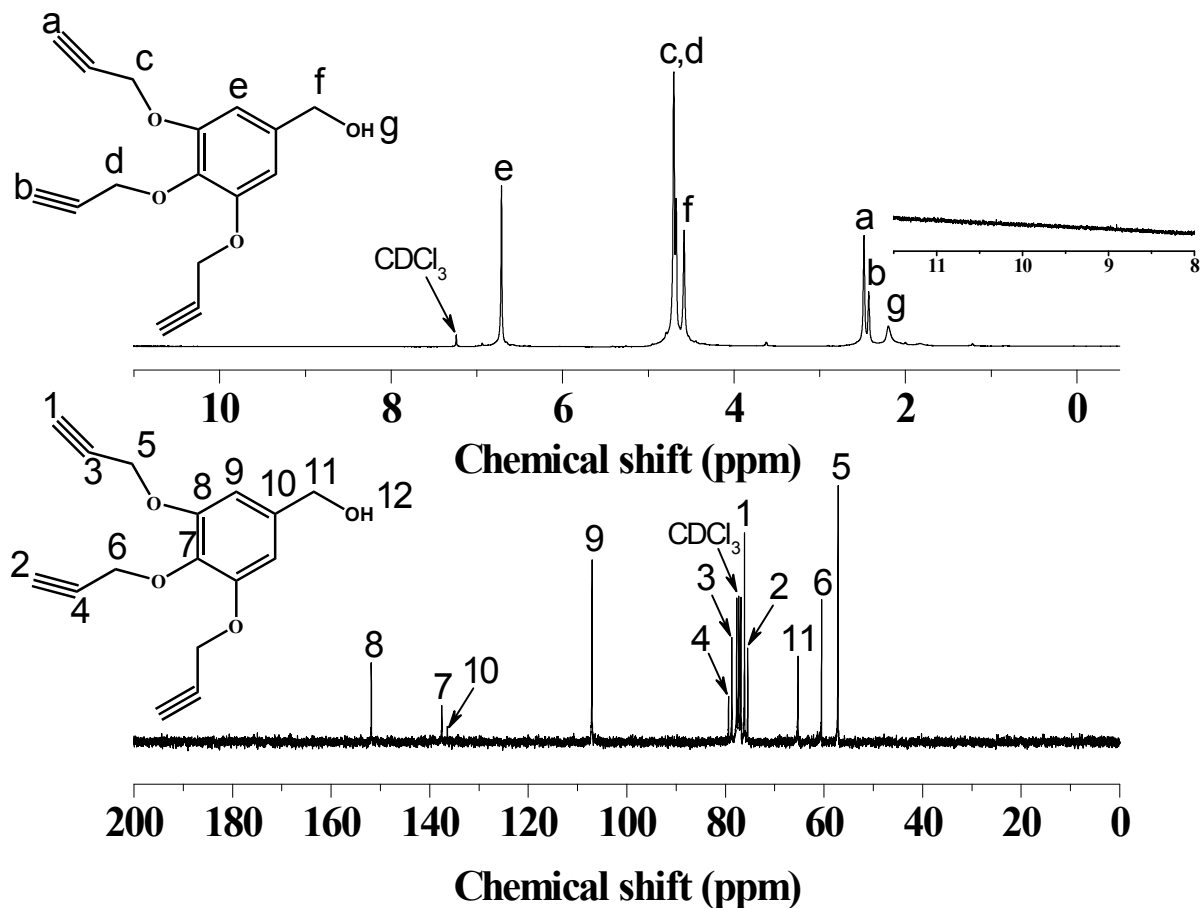


Figure S3. ¹H NMR and ¹³C NMR spectra of compound (3) in CDCl₃.

Synthesis of Tripropargyl PLLA (4)

Polymerization was carried out at 140 °C in anhydrous toluene in a dried glass reactor; 3,6-dimethyl-1,4-dioxane-2,5-dione (10 g, 70 mol), (3) (0.13 g, 0.46 mmol) and tin(II) 2-ethylhexanoate (0.37 g, 0.9 mmol) were sequentially added to the reactor via chemical feeding equipment. After 16 h of polymerization, excess acetic chloride (0.71 ml, 0.8 g, 10 mmol) was added and the polymer was recovered by precipitation in cold methanol. The monomer conversion was 78% to Tripropargyl PLLA (7.8 g).

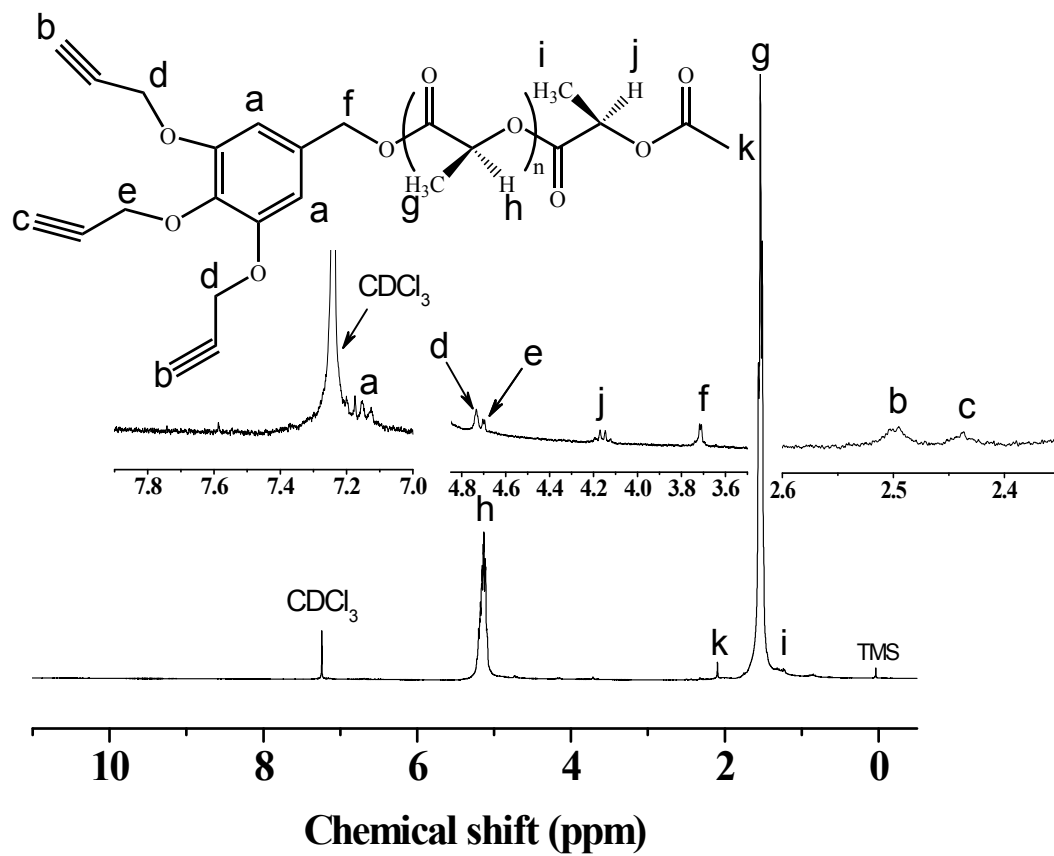


Figure S4. ^1H NMR spectrum of Tripropargyl PLLA (4) in CDCl_3 .

Synthesis of TriPOSS-PLLA

Mono-benzyl azide POSS (N₃-POSS) was synthesized by reacting sodium azide with mono-benzyl chloride POSS according to a previously described procedure.²⁹ Tri-alkyne end-capped (**4**) (5 g, 0.25 mmol) and azide-labeled N₃-POSS (1.0 g, 1.1 mmol) were dissolved in THF (40 ml) and the resulting solution was purged with dry argon for 5 min. Pentamethyldiethylenetriamine (PMDETA, 25 μ L, 120 μ mol) and copper(I) bromide (CuBr, 20 mg, 142 μ mol) were added to the reaction solution, then the solution was degassed through three freeze/thaw evacuation cycles. The reaction mixture was heated to 50 °C for 16 h under nitrogen, cooled to room temperature, passed through an Al₂O₃ column, distilled under reduced pressure and the product was purified by precipitation in hexane to completely remove excess N₃-POSS. Yield: 96 % (4.9 g).

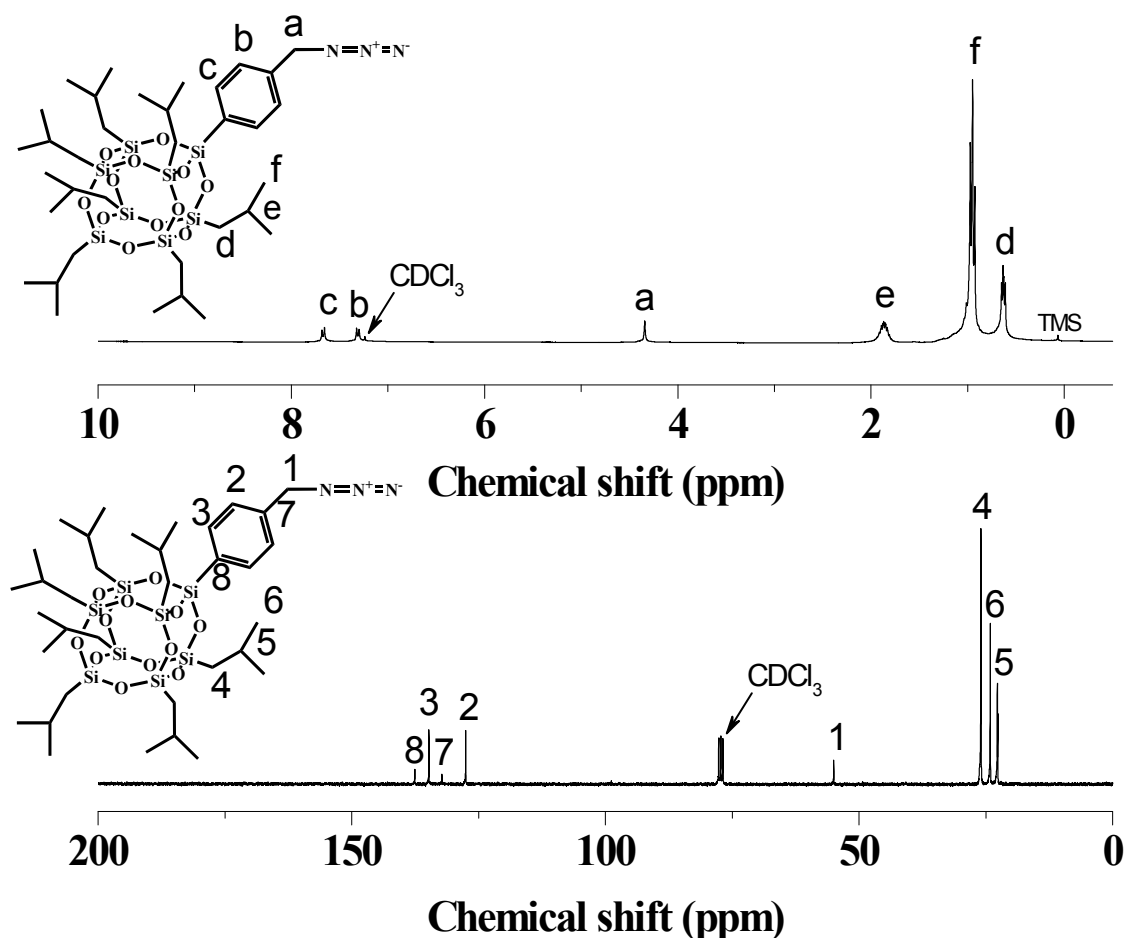


Figure S5 ¹H NMR and ¹³C NMR spectra of N₃-POSS in CDCl₃.

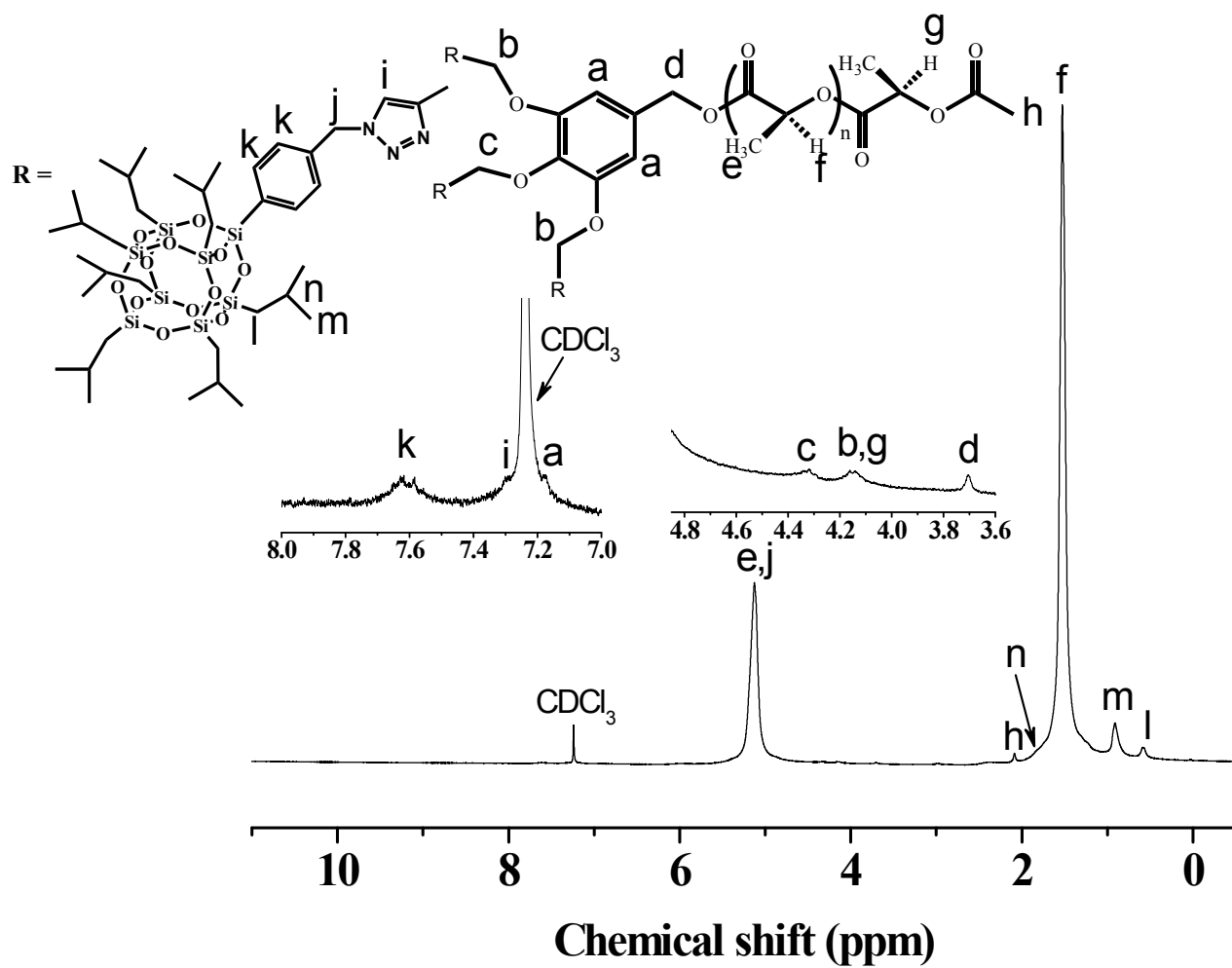


Figure S6. ^1H NMR spectrum of TriPOSS-PLLA (5) in CDCl_3 .

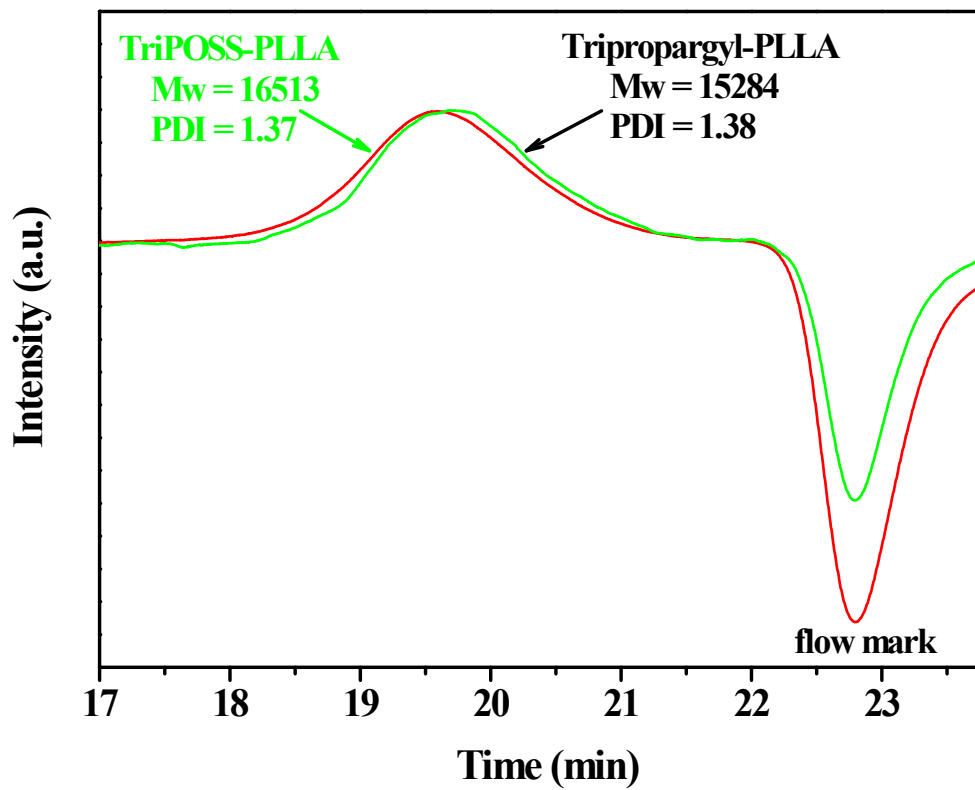
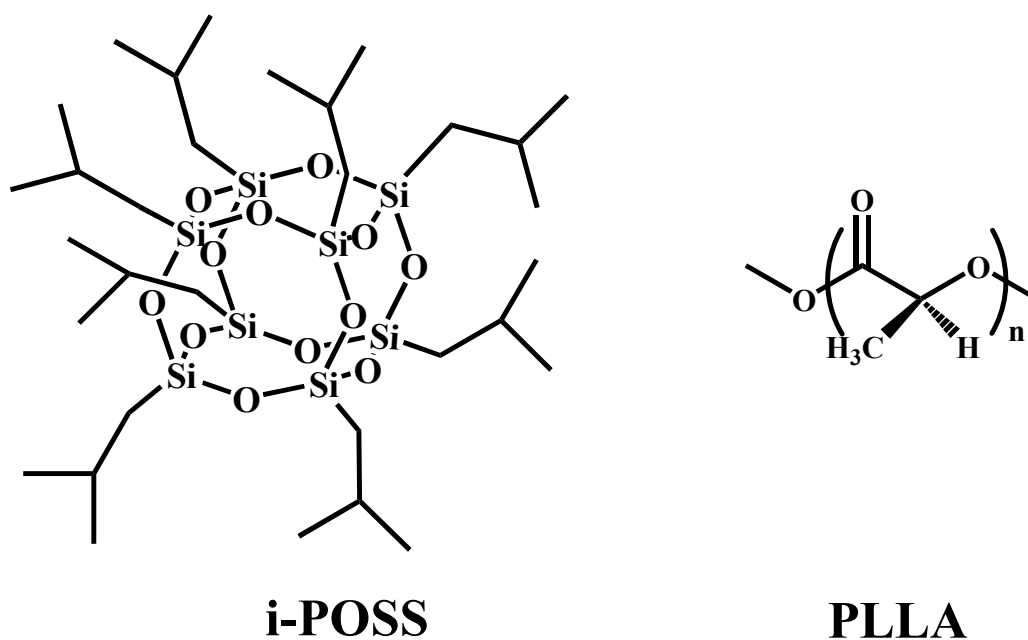


Figure S7. GPC traces for TriPOSS-PLLA and Tripropargyl PLLA.



Scheme S2. Structural representations of i-POSS and PLLA.

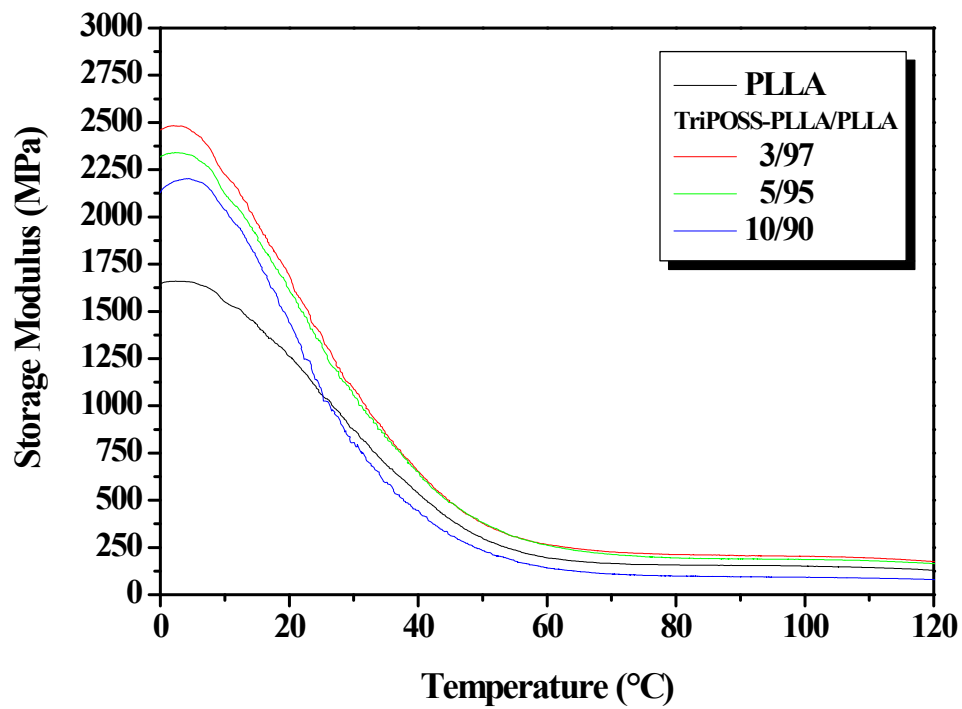


Figure S8. DMA curves for the TriPOSS-PLLA/PLLA system.

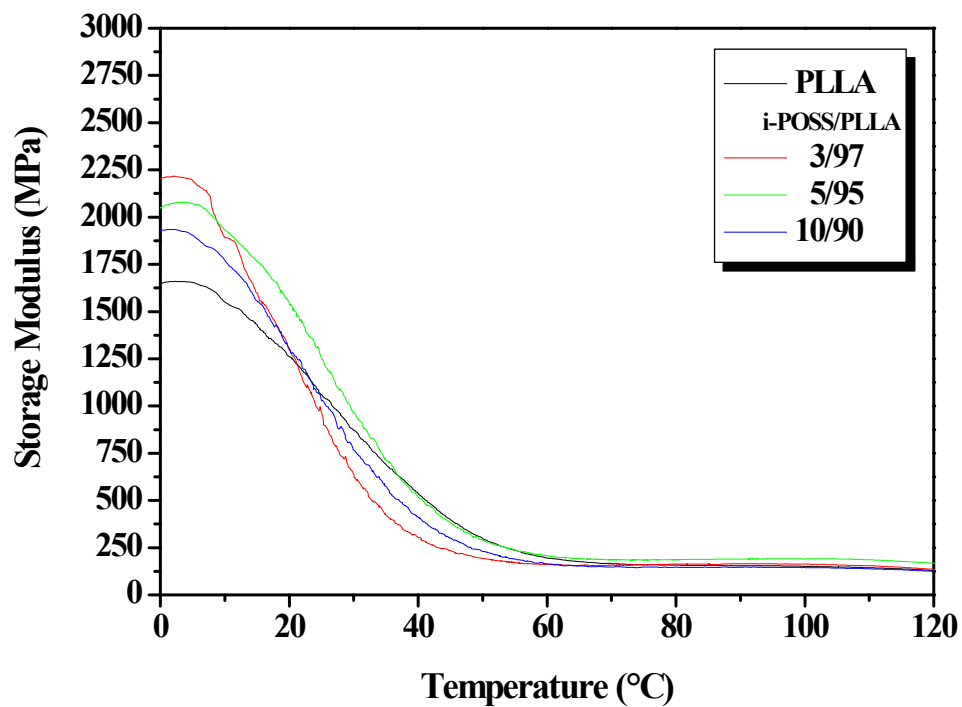


Figure S9. DMA curves for the i-POSS/PLLA system.

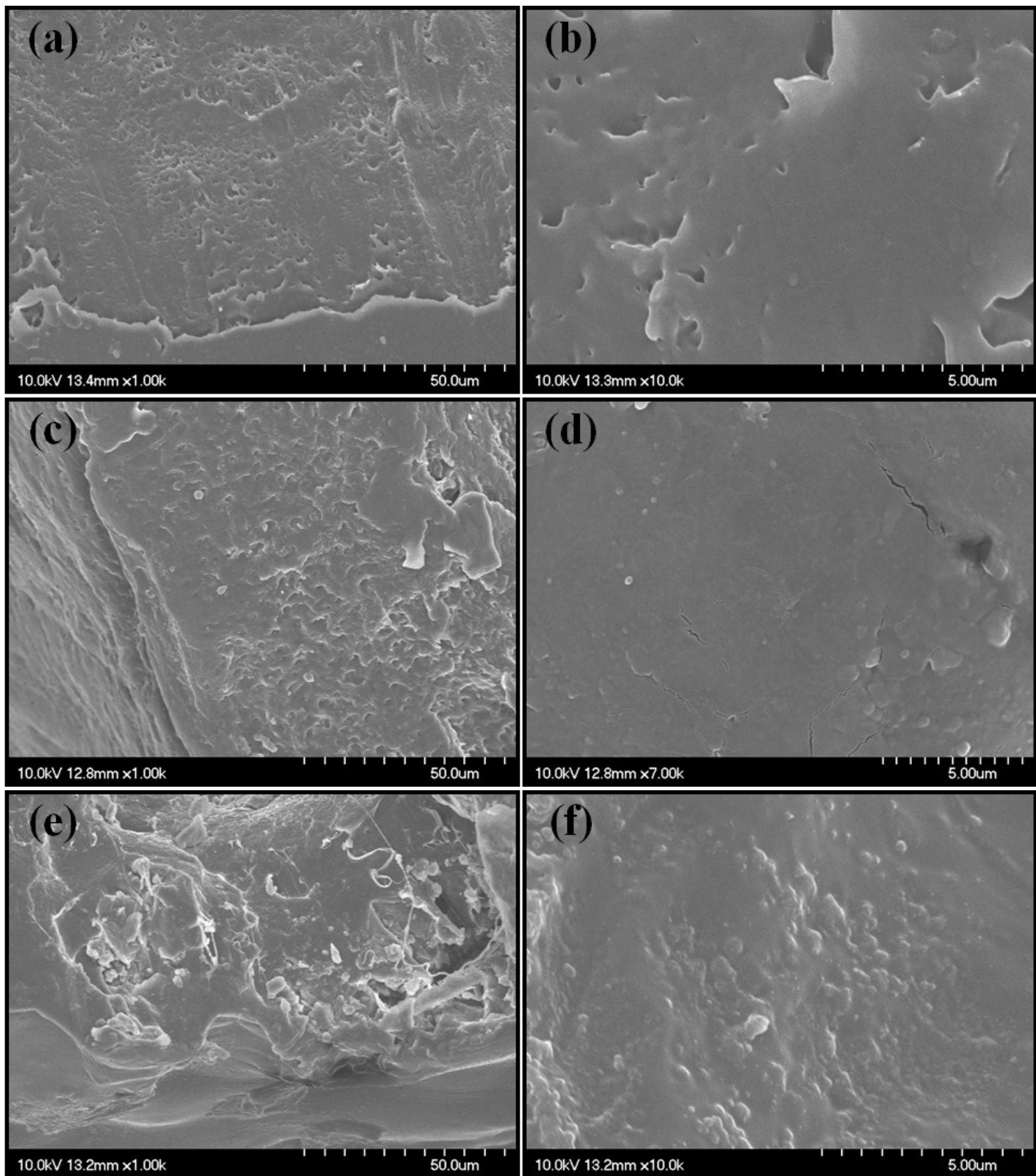


Figure S10. SEM images of cross-sections of (a, b) pristine PLLA, (c, d) 10/90 TriPOSS-PLLA/PLLA and (e, f) 10/90 i-POSS/PLLA composites.

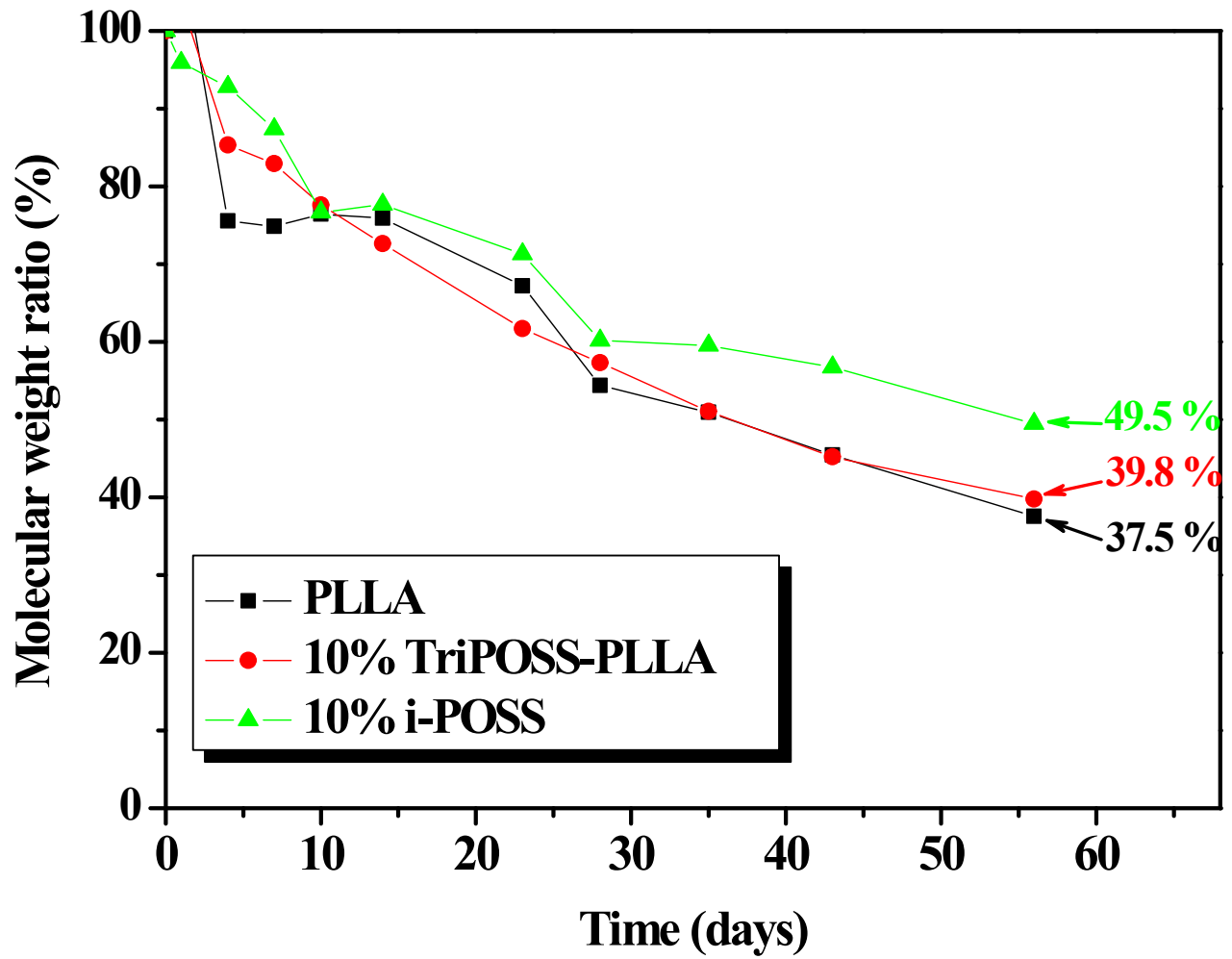


Figure S11. Time-dependence of hydrolytic degradation of pristine PLLA, 10/90 TriPOSS-PLLA/PLLA and 10/90 i-POSS/PLLA films.

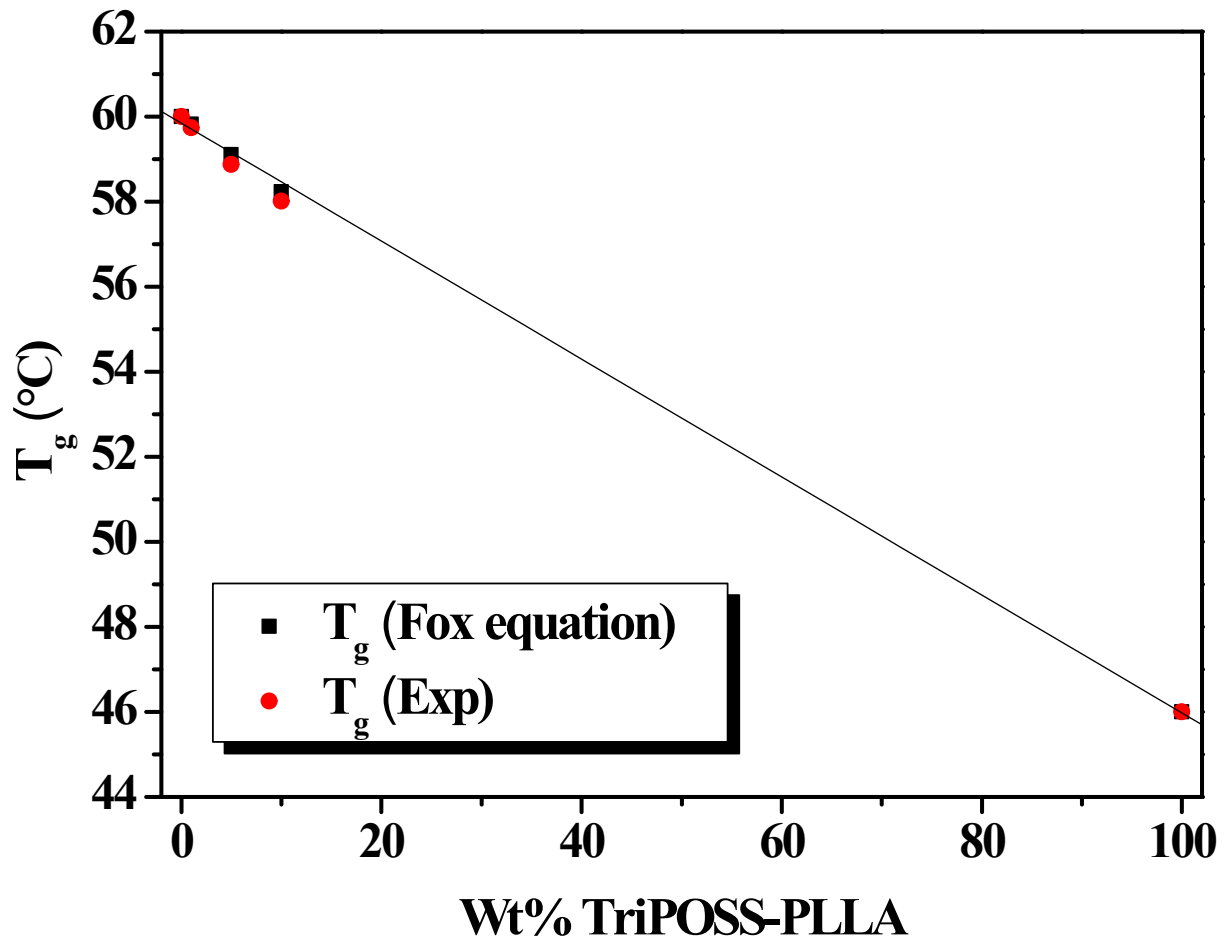


Figure S12. Comparison of experimental (from DSC) and Fox-equation-calculated T_g values for TriPOSS-PLLA/PLLA system.