Supporting Information

Biodegradable and Crosslinkable Poly(propylene fumarate) Liquid Crystal Polymers

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Materials

Maleic anhydride (MAn), glycidol, cholesteryl chloroformate, 4-dimethylaminopyridine (DMAP), triethylamine (Et_3N), diethylamine (Et_2NH), bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) and chromium salen were purchased from Aladdin Inc. Anhydrous dichloromethane (CH_2Cl_2), hexane, methanol and tetrahydrofuran (THF) were purchased from Energy Chemical Inc.

General characterization

All ^1H NMR spectra and ^{13}C NMR spectra were obtained from a Bruker HW600 MHz spectrometer (AVANCE AV-600), using $CDCl_3$ (δ 7.26 ppm) as the solvent. Molecular weights of two PPF-LCPs were measured using gel permeation chromatography (GPC, Agilent PL-GPC50) with tetrahydrofuran (THF) as the mobile phase at 40 ^oC.

Polarized optical microscopy (POM) equipped with an Olympus BX53P microscope and a Mettler PF82HT hot stage were used to observe the mesomorphic properties of monomers and polymers.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7 under nitrogen atmosphere at a heating rate of 10 ^oC/min. Differential scanning calorimetry (DSC) spectra were obtained on a TA Q200 instrument under nitrogen atmosphere at both heating and cooling rates of 20 ^oC/min. One-dimensional and two-dimensional small-angle X-ray scattering (SAXS) patterns were recorded on a high-flux small angle

X-ray scattering instrument (SAXSess, Anton Paar) equipped with a Kratky block-collimation system and a temperature control unit (Anton Paar TCS300).

The tensile tests were performed on a dynamic mechanical analyzer (DMA 850, TA Instrument). The stress-strain curves of PPF-LCP films with a dimension of ca. 15 mm long × 5.0 mm wide × 0.30 mm thick were measured at 30 °C during the tensile force rose to 5.0 N at a rate of 0.05 N/min.

Experimental section

Synthesis of the biodegradable and crosslinkable PPF-LCP1. (1) Glycidol (1.50 g, 20.25 mmol), DMAP (0.49 g, 4.05 mmol) and anhydrous CH_2Cl_2 (50 mL) were added into a three-necked flask. The reaction mixture was stirred at 0 °C for 10 min, followed by injection of triethylamine (Et_3N, 3.07 g, 30.38 mmol) and CH_2Cl_2 (50 mL) solution of cholesteryl chloroformate (13.64 g, 30.38 mmol) respectively. Then the above solution was allowed to stir at room temperature for 24 h. After removing the solvent, the residue was purified by column chromatography (ethyl acetate/petroleum ether, v/v, 1:30) to provide compound **3** as a white powder (7.50 g, yield: 78.3%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.40-5.38 (m, 1H), 4.51-4.45 (m, 1H), 4.36 (dd, J = 12.1, 3.4 Hz, 1H), 4.03 (dd, J = 12.1, 6.1 Hz, 1H), 3.23 (m, 1H), 2.87-2.82 (m, 1H), 2.66 (dd, J = 4.9, 2.6 Hz, 1H), 2.44-2.34 (m, 2H), 2.03-1.79 (m, 6H), 1.70-1.41 (m, 9H), 1.39- 1.22 (m, 5H), 1.19-1.05 (m, 8H), 1.02-0.99 (m, 4H), 0.91 (d, J = 6.5 Hz, 3H), 0.86 (dd, J = 6.6, 2.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 154.30, 139.24, 123.06, 78.30, 77.26, 77.05, 76.83, 67.96, 56.70, 56.15, 50.01, 49.09, 44.64, 42.32, 39.73, 39.53, 37.99, 36.85, 36.54, 36.20, 35.80, 31.88, 28.24, 28.02, 27.67, 24.29, 23.84, 22.83, 22.58, 21.05, 19.27, 18.73, 11.87. ESI-MS m/z: 509.36 $[M + Na]^+$.

(2) Maleic anhydride (MAn) (350 mg, 3.57 mmol), compound **3** (950 mg, 2.01 mmol), chromium salen (6.30 mg, 0.01 mmol) and anhydrous hexane (0.72 mL) was added into a 10 mL dried Schlenk flask. The flask was degassed and exchanged with high-purity nitrogen for three cycles, and then the mixture was stirred at 55 °C for 20 h. After evaporation of the solvent, the residue was dissolved in a little amount of CH_2Cl_2 and precipitated into an excess of hexane for three times. The gathered product

was further dried in vacuum for 24 h to give the copolymer **PPM-LCP1** (**5**) (740 mg, yield: 59.9%) as a yellow powder. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.30 (s, 2H), 5.38 (s, 2H), 4.55-4.12 (m, 6H), 2.43-2.32 (m, 2H), 1.97 (d, *J* = 27.2 Hz, 6H), 1.69-1.41 (m, 8H), 1.40-1.21 (m, 6H), 1.19-1.03 (m, 8H), 1.00 (s, 4H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 164.41, 154.08, 139.25, 129.94, 123.07, 78.57, 77.25, 77.04, 76.83, 70.05, 64.98, 62.72, 56.70, 56.18, 49.99, 42.33, 39.74, 39.53, 37.93, 36.84, 36.54, 36.21, 35.83, 31.88, 31.61, 28.25, 27.82, 24.30, 23.88, 22.84, 22.63, 21.06, 19.29, 18.74, 14.15, 11.88.

(3) Compound **5** (200 mg, 0.32 mmol) was dissolved in 0.5 mL of $CHCl_3$ in a 10 mL round-bottom flask and then diethylamine (Et_2NH, 2.0 mg, 0.03 mmol) was carefully added into the above solution. The reaction solution was allowed to stir at room temperature for 20 h. After completion of reaction, the solvent was removed by rotary evaporation. The residue was subsequently redissolved in CH_2Cl_2 and precipitated into hexane to provide the isomerized copolymer **PPF-LCP1** (**6**) (190 mg, yield: 95.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.88 (s, 2H), 5.39 (s, 2H), 4.75-4.08 (m, 6H), 2.38 (s, 2H), 1.90 (m, 6H), 1.71-1.41 (m, 8H), 1.40-1.22 (m, 7H), 1.11 (m, 7H), 1.03-0.96 (m, 4H), 0.96-0.82 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 162.67, 161.69, 153.05, 147.11, 138.14, 132.41, 123.64, 122.13, 55.68, 55.15, 48.98, 41.31, 38.71, 38.51, 36.91, 35.81, 35.52, 35.18, 34.78, 30.89, 30.83, 30.64, 27.21, 27.00, 26.59, 23.27, 22.84, 21.81, 21.55, 20.04, 18.25, 17.71, 10.85.

Synthesis of the biodegradable and crosslinkable PPF-LCP2. (1) 2-(2-(Oxiran-2-ylmethoxy)ethoxy)ethanol (1.95 g, 12.02 mmol), DMAP (0.29 g, 2.37 mmol) and anhydrous CH_2Cl_2 (50 mL) were added into a three-necked flask. The reaction mixture was stirred at 0 °C for 10 min, followed by injection of triethylamine (Et_3N, 1.82 g, 17.98 mmol) and CH_2Cl_2 (50 mL) solution of cholesteryl chloroformate (8.09 g, 18.01 mmol) respectively. Then the above solution was allowed to stir at room temperature for 24 h. After removing the solvent, the residue was purified by column chromatography (ethyl acetate/petroleum ether, v/v, 1:20) to provide compound **8** as a white powder (4.45 g, yield: 64.4%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.40-5.37 (m, 1H), 4.50-4.44 (m, 1H), 4.27 (dd, *J* = 5.5, 4.1 Hz, 2H), 3.79 (dd, *J* = 11.7, 3.0 Hz, 1H), 3.75-

3.63 (m, 6H), 3.43 (dd, *J* = 11.7, 5.9 Hz, 1H), 3.16 (m, 1H), 2.81-2.78 (m, 1H), 2.61 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.43-2.33 (m, 2H), 2.08-1.77 (m, 6H), 1.69-1.40 (m, 8H), 1.40-1.22 (m, 7H), 1.18-1.03 (m, 7H), 1.01 (d, *J* = 4.9 Hz, 4H), 0.91 (t, *J* = 5.9 Hz, 3H), 0.88-0.82 (m, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 154.53, 139.36, 122.96, 77.96, 77.25, 77.04, 76.83, 72.03, 70.70, 69.02, 66.66, 56.70, 56.14, 50.84, 50.00, 44.27, 42.32, 39.73, 39.53, 38.03, 36.86, 36.55, 36.19, 35.80, 31.88, 28.24, 28.03, 27.69, 24.29, 23.84, 22.84, 22.58, 21.05, 19.28, 18.73, 11.87. ESI-MS m/z: 597.41 $[M + Na]^+$.

(2) Maleic anhydride (MAn) (152 mg, 1.55 mmol), compound **8** (500 mg, 0.87 mmol), chromium salen (2.50 mg, 0.004 mmol) and anhydrous hexane (0.31 mL) was added into a 10 mL dried Schlenk flask. The flask was degassed and exchanged with high-purity nitrogen for three cycles, and then the mixture was stirred at 55 °C for 20 h. After evaporation of the solvent, the residue was dissolved in a little amount of CH_2Cl_2 and precipitated into an excess of hexane for three times. The gathered product was further dried in vacuum for 24 h to give the copolymer **PPM-LCP2** (**9**) (340 mg, yield: 55.6%) as a yellow powder. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.32 (s, 2H), 5.34 (d, *J* = 54.3 Hz, 2H), 4.50-4.20 (m, 5H), 3.81-3.51 (m, 8H), 2.38 (t, *J* = 9.5 Hz, 2H), 2.05-1.77 (m, 5H), 1.68-1.40 (m, 7H), 1.39-1.22 (m, 11H), 1.19-1.04 (m, 7H), 1.02-0.97 (m, 5H), 0.89 (dd, *J* = 15.0, 6.7 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 164.66, 164.11, 154.53, 139.36, 136.52, 122.97, 77.98, 70.88, 70.51, 69.11, 66.64, 66.41, 63.28, 56.70, 56.16, 50.00, 42.32, 39.73, 39.53, 38.02, 36.86, 36.55, 36.20, 35.81, 31.88, 31.60, 28.24, 28.02, 27.69, 24.29, 23.86, 22.83, 22.62, 21.06, 19.29, 18.73, 14.13, 11.87.

(3) Compound **9** (150 mg, 0.21 mmol) was dissolved in 0.3 mL of $CHCl_3$ in a 10 mL round-bottom flask and then diethylamine (Et_2NH, 1.5 mg, 0.02 mmol) was carefully added into the above solution. The reaction solution was allowed to stir at room temperature for 20 h. After completion of reaction, the solvent was removed by rotary evaporation. The residue was subsequently redissolved in CH_2Cl_2 and precipitated into hexane to provide the isomerized copolymer **PPF-LCP2** (**10**) (136 mg, yield: 90.6%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 6.88 (s, 2H), 5.41-5.32 (m, 2H), 4.46-4.24 (m, 5H), 3.71-3.63 (m, 8H), 2.42-2.32 (m, 2H), 1.96-1.79 (m, 5H), 1.58-1.44 (m, 7H), 1.41-1.14 (m, 11H), 1.14-1.06 (m, 7H), 0.99 (d, *J* = 11.9 Hz, 5H), 0.94-0.88

(m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 167.73, 164.29, 154.50, 139.35, 135.77, 129.64, 122.96, 71.04, 70.55, 69.05, 66.62, 56.69, 56.14, 49.99, 42.89, 42.32, 42.09, 39.72, 39.52, 38.02, 36.85, 36.54, 36.19, 35.80, 31.91, 31.84, 31.60, 28.24, 28.02, 27.68, 24.29, 23.84, 22.84, 22.67, 22.58, 21.05, 19.28, 18.73, 14.14, 14.07, 12.72, 11.87, 11.36.

Synthesis of the crosslinked PPF-LCPs. PPF-LCPs (1eq) and BAPO (0.01eq) were dissolved in 0.5 mL of THF and then photocrosslinked in the LC region for 30 min under the 365 nm UV light to provide the crosslinked PPF-LCPs.

In vitro **degradation experiments of polymer films.** The dumbbell-shaped polymer film was weighed, and then immersed in 20 mL of 0.1 mol/L phosphate buffer solution (PBS, pH~7.4) and placed in an oven at 37 °C. Throughout the experiment, the PBS was replaced with fresh solution every day. At each time point (days 0, 5, 10, 15 and 20), the solution was removed, and the film was dried in a vacuum oven at 37 °C for 12 h, and then weighed. The weight loss was calculated by the formula: $(M_0-M_t)/M_0$ (M_0 is the initial weight, M_t is the final weight at a certain time).

Table S1 Characterization data of the PPM-LCPs synthesized by ring open polymerization

Entry	Monomer	[MAn]:[Monomer]:[Cat][a]	Polymer	Reaction time (h)	Monomer conversion (%)[b]	Yield (%)[c]
1	Monomer **3**	200:200:1	PPM-LCP1	20	52	32
2	Monomer **8**	200:200:1	PPM-LCP2	20	33	18
3	Monomer **3**	356:200:1	PPM-LCP1	10	39	23
4	Monomer **3**	356:200:1	PPM-LCP1	20	84	58
5	Monomer **8**	356:200:1	PPM-LCP2	10	82	51
6	Monomer **8**	356:200:1	PPM-LCP2	20	88	55
7	Monomer **3**	500:200:1	PPM-LCP1	20	78	49
8	Monomer **8**	500:200:1	PPM-LCP2	20	86	53

[a]Reaction conditions: [Monomer] = 2.8 M in hexanes, T = 55 °C. [b]Determined by ^1H NMR spectrum of the crude product. [c]Isolated yield.

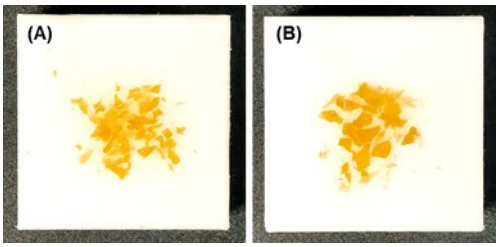

Figure S1. (A) PPM-LCP1 and (B) PPM-LCP2 samples showing poor mechanical performances.

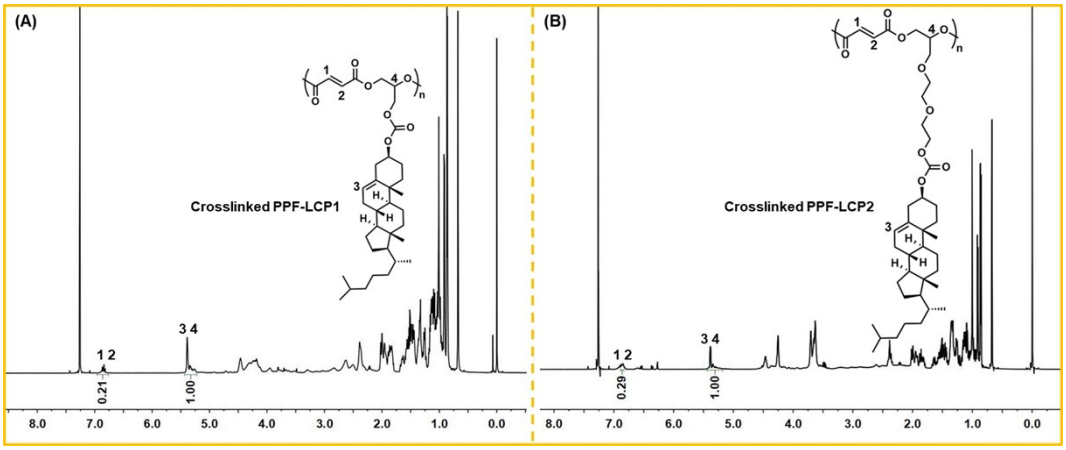

Figure S2. [1]H NMR spectra of (A) crosslinked PPF-LCP1 and (B) crosslinked PPF-LCP2.

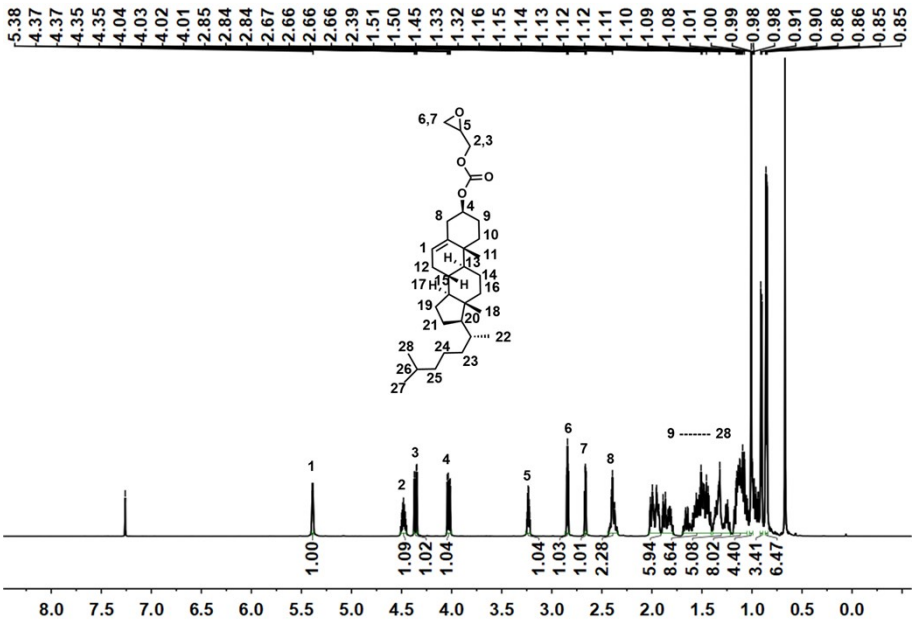

Figure S3. [1]H-NMR spectrum of monomer **3**.

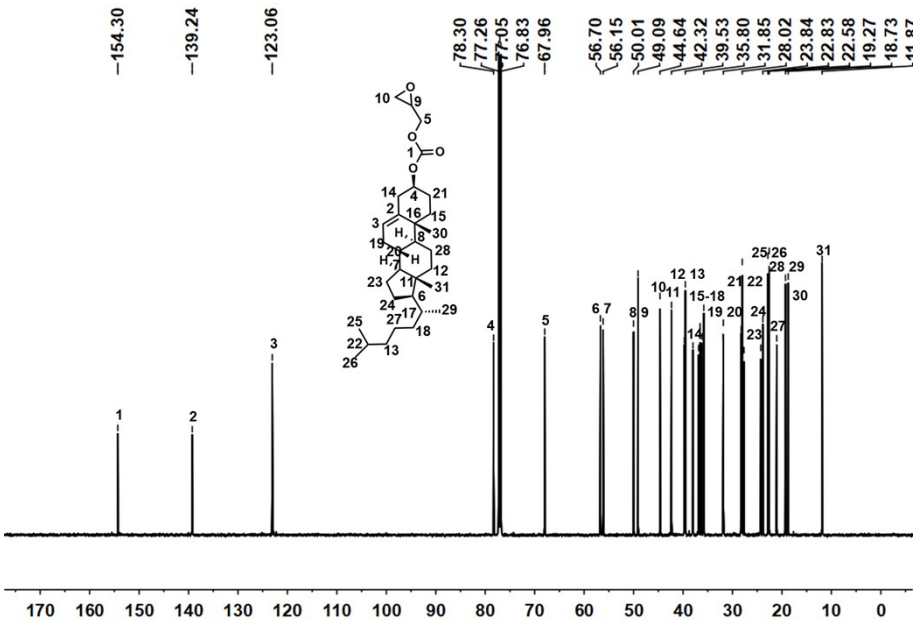

Figure S4. ^{13}C-NMR spectrum of monomer **3**.

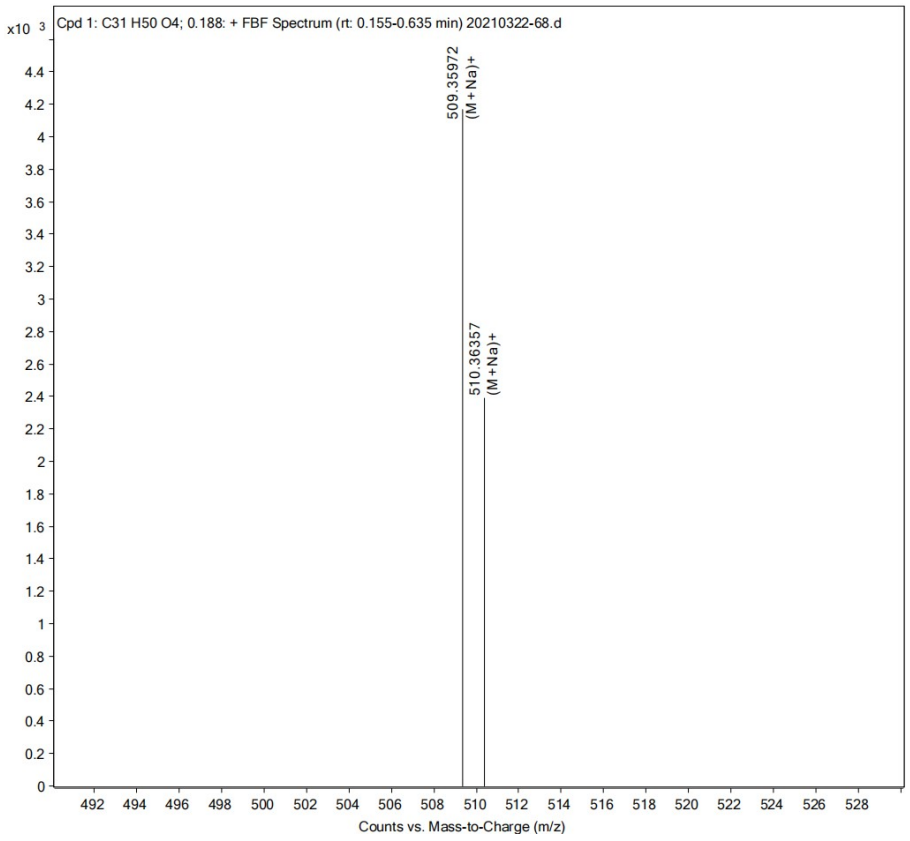

Figure S5. ESI-MS spectrum of monomer **3**.

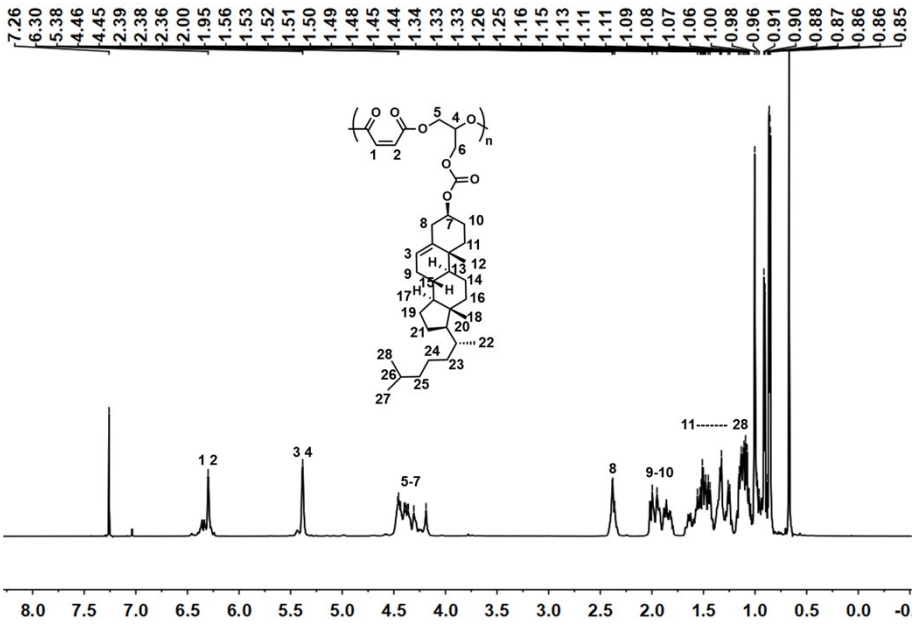

Figure S6. ^{1}H-NMR spectrum of PPM-LCP1 (**5**).

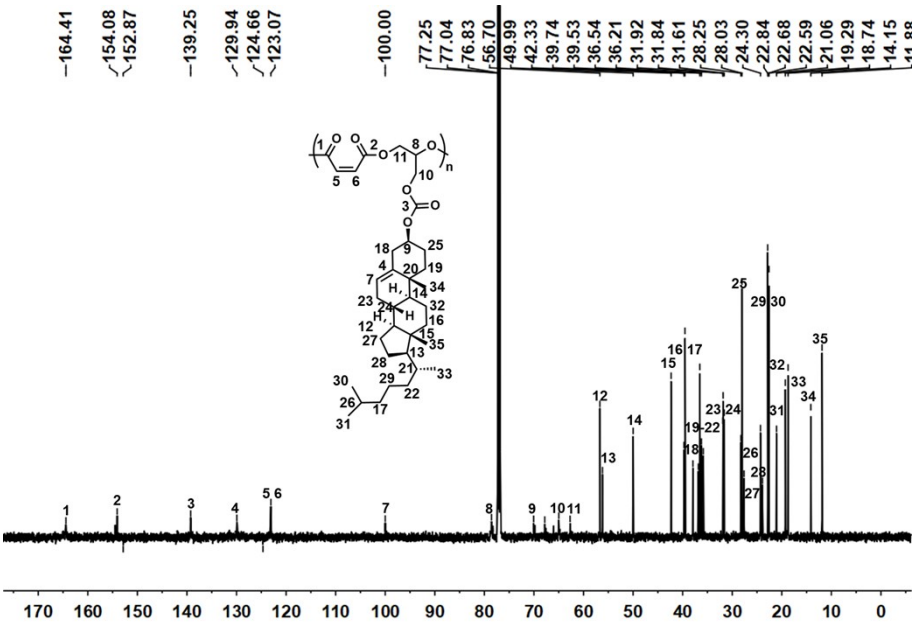

Figure S7. ^{13}C-NMR spectrum of PPM-LCP1 (**5**).

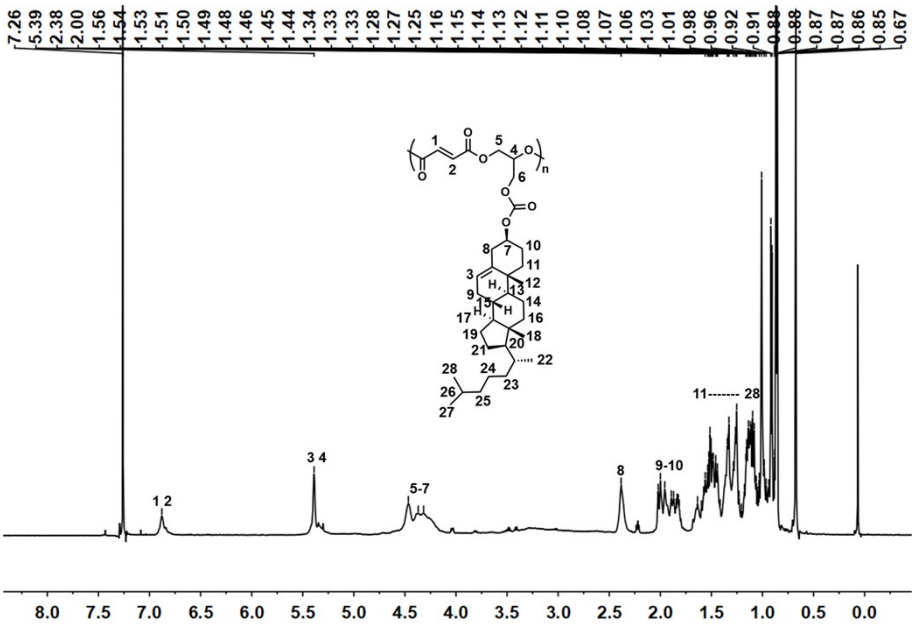

Figure S8. ^{1}H-NMR spectrum of PPF-LCP1 (**6**).

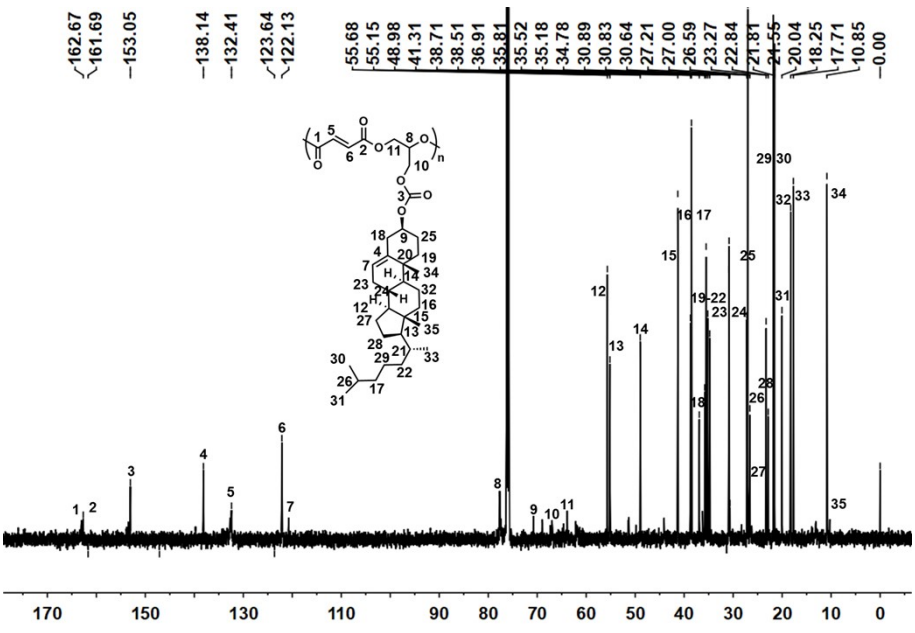

Figure S9. ^{13}C-NMR spectrum of PPF-LCP1 (**6**).

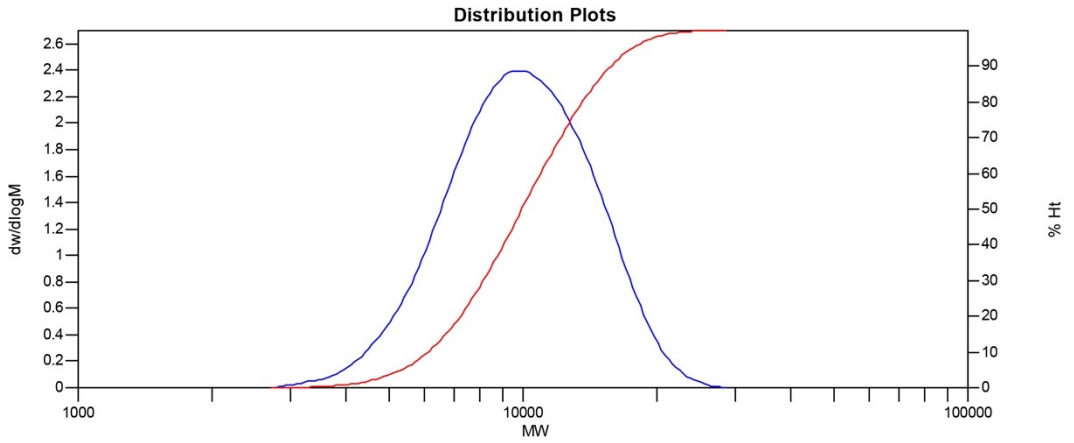

Figure S10. Molecular mass distribution plots of PPF-LCP1 (**6**).

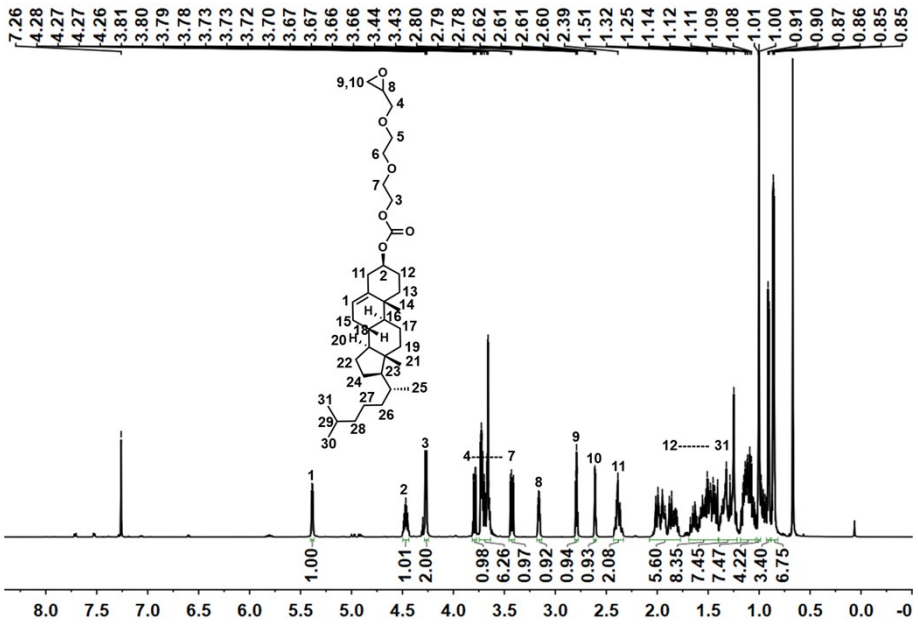

Figure S11. [1]H-NMR spectrum of monomer (**8**).

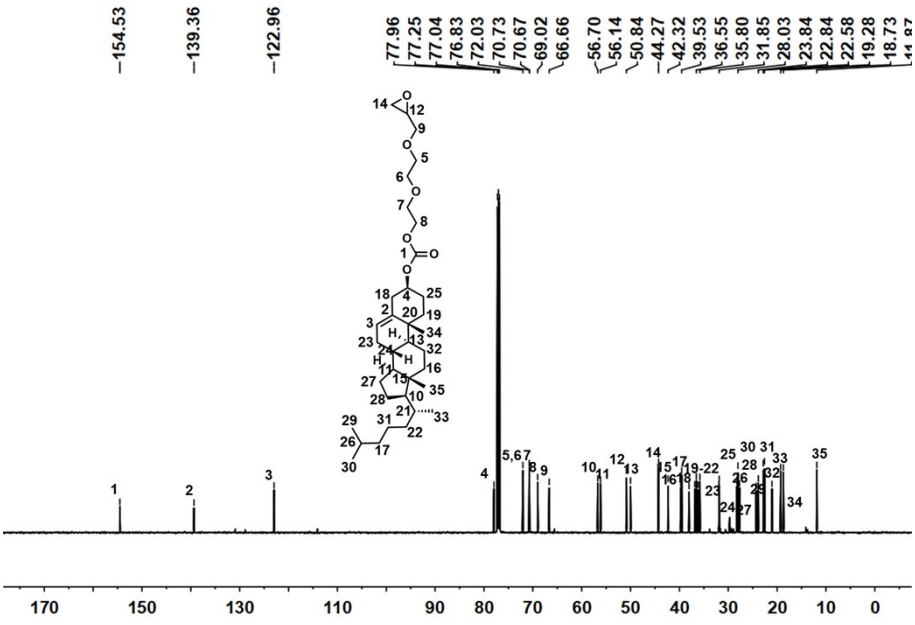

Figure S12. ^{13}C-NMR spectrum of monomer (**8**).

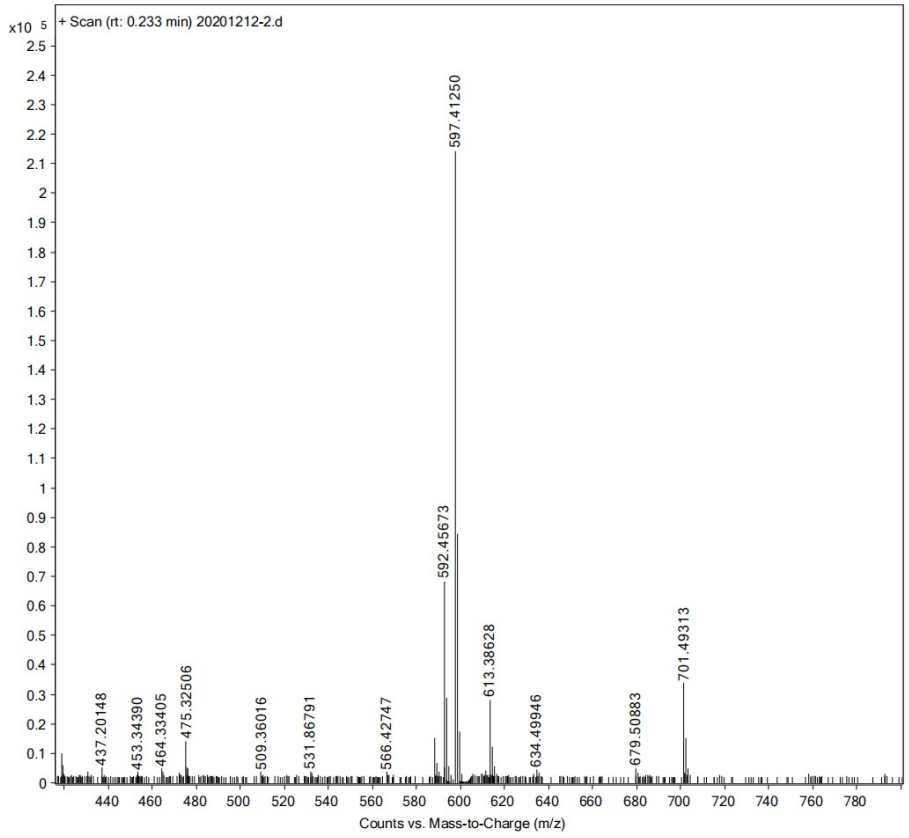

Figure S13. ESI-MS spectrum of monomer (**8**).

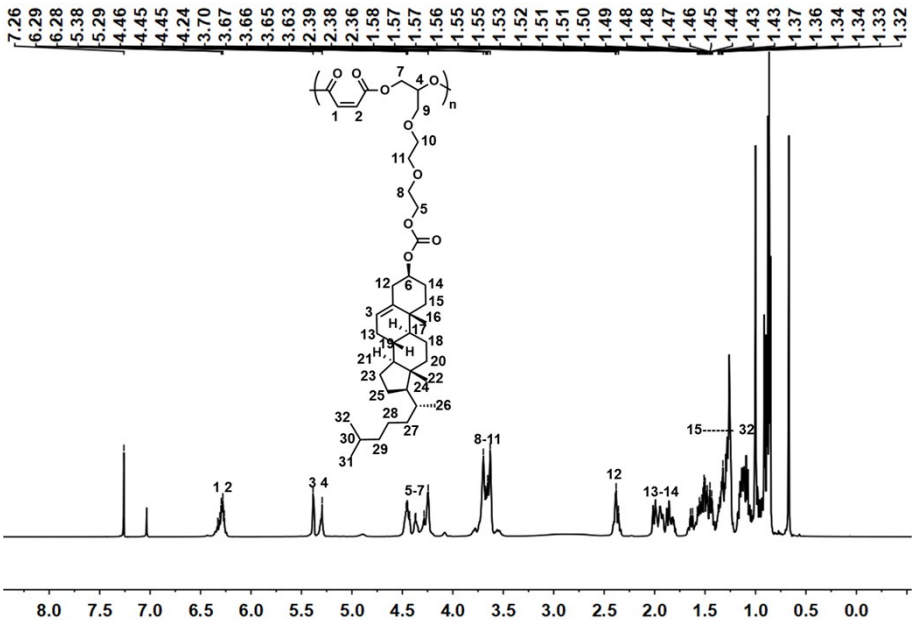

Figure S14. ^{1}H-NMR spectrum of PPM-LCP2 (**9**).

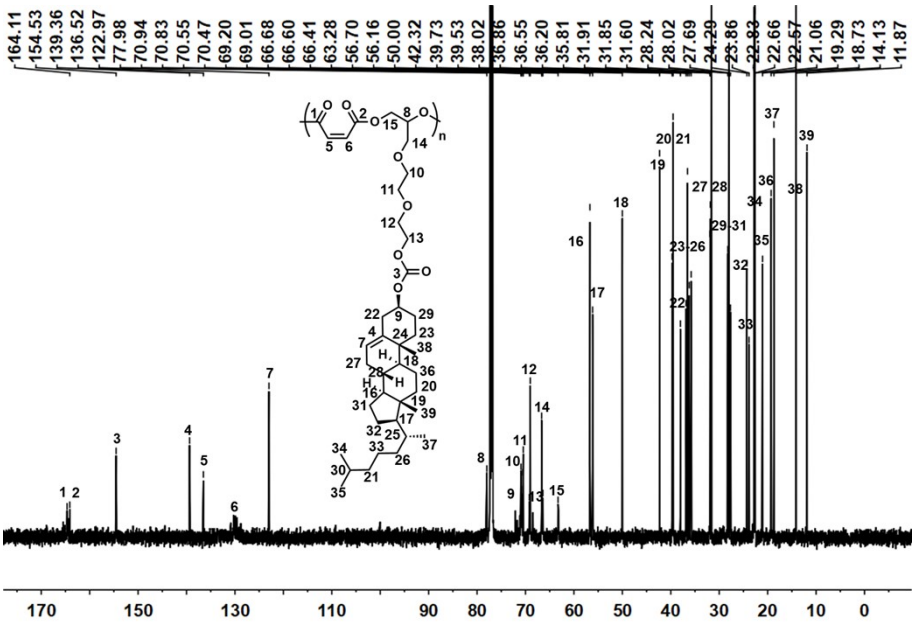

Figure S15. ^{13}C-NMR spectrum of PPM-LCP2 (**9**).

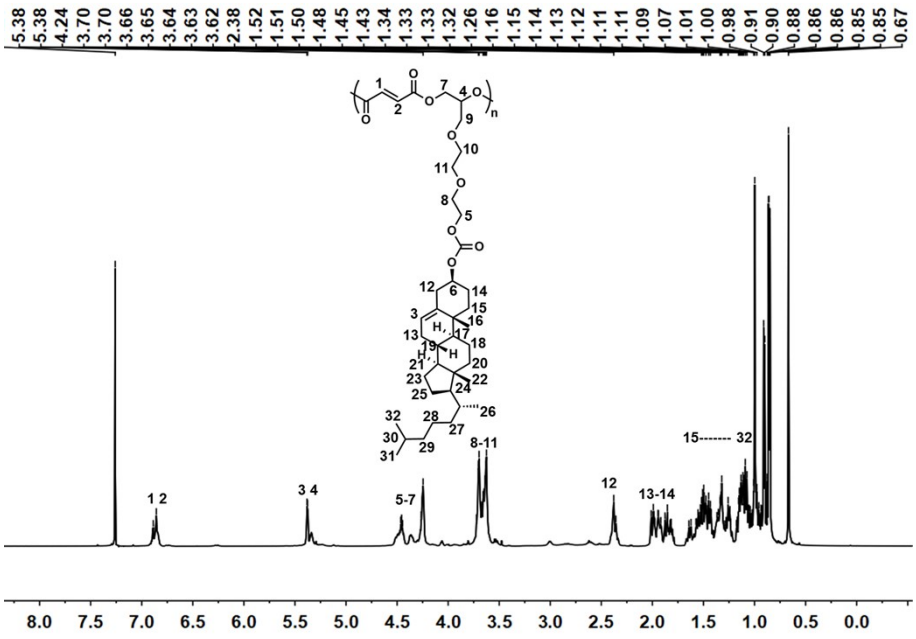

Figure S16. ^{1}H-NMR spectrum of PPF-LCP2 (**10**).

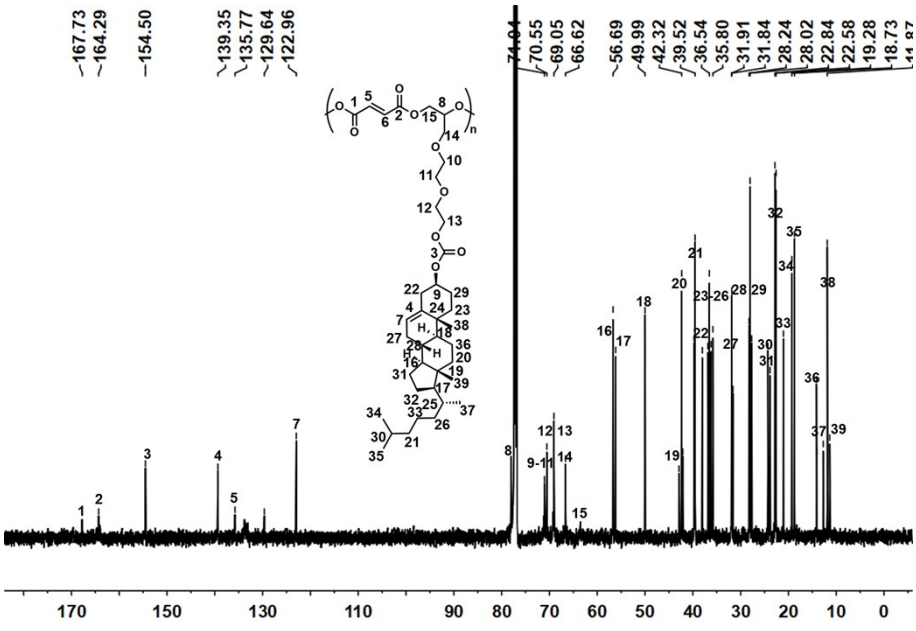

Figure S17. ^{13}C-NMR spectrum of PPF-LCP2 (**10**).

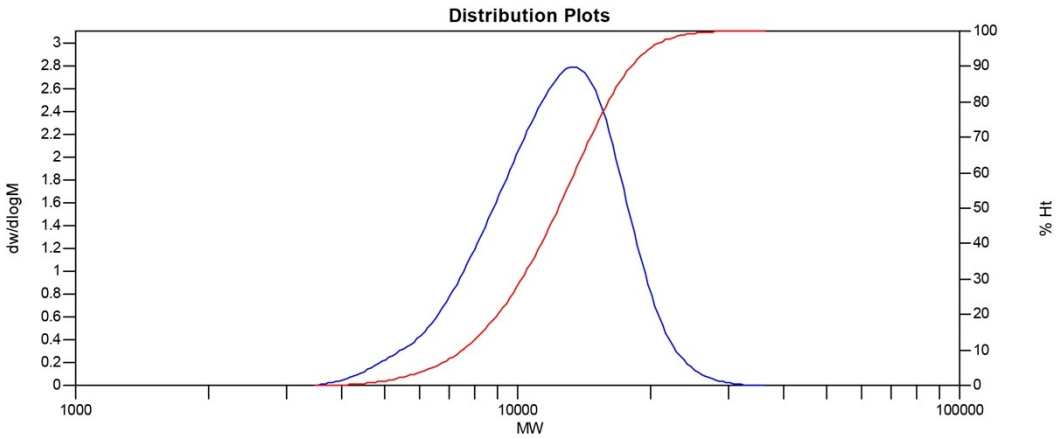

Figure S18. Molecular mass distribution plots of PPF-LCP2 (**10**).