Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary information for:

A Click Chemistry Approach to the Efficient Synthesis of Polyoxometalate-Polymer Hybrids with Well-defined Structures

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Materials and methods:

Tin (II) 2-ethylhexanoate ($Sn(Oct)_2$; 96%) and ε-caprolactone (ε-CL; 99%) were purchased from Aldrich and ascorbic acid (99%) and 4-(chloromethyl)phenyltrimethoxysilane (90%) were purchased from Alfa Aesar. Other reagents were purchased from major chemical supplies and used as received unless otherwise noted. ε-CL monomer and toluene were dried over CaH_2 and distilled before used. $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 10H_2O$

was synthesized according to the literature procedure.[1]

^{1}H NMR spectra were recorded on a Varian UNITY plus-400 spectrometer in dimethylsulfoxide-d_6 (DMSO-d_6) and chemical shifts are given in ppm, referenced to the residual resonances of the solvents (δ = 2.50 for DMSO-d_6). ^{31}P (121.5 MHz) NMR spectra were obtained by use of a Varian Mercury Vx-300 spectrometer in DMSO-d_6 at a concentration of 30mg/0.5ml. The molecular mass of compound **2** was taken on an electrospray ionization time-of-flight (ESI-TOF) mass spectrometer (X7ICP-MS). IR spectra were taken on a FT-IR spectrometer (Bio-Rad FTS-135) sampled with KBr pellet samples. Size exclusion chromatography (SEC) was carried out in THF (flow rate: 1 ml/min) at 35°C with a Waters 515 HPLC pump equipped with a Waters 2414 refractive index detector and three Waters Ultrastyragel columns. Polystyrene standards were used for calibration. Thermogravimetric analysis (TGA) data was collected on Netzsch STA449F3 under argon with a rate of 10 °C /min in the range of 25–700°C. The spectra of energy dispersive X-ray spectroscopy (EDX) were recorded using EDAX Genesis Apollo 10 operated under an acceleration voltage of 30 kV.

Synthesis of $(NBu_4)_6[\alpha_2$-$P_2W_{17}O_{61}(SiC_6H_4CH_2Cl)_2O]$: 1

According to the procedure reported in Ref. 2, we synthesized $(NBu_4)_6[\alpha_2$-$P_2W_{17}O_{61}(SiC_6H_4CH_2Cl)_2O]$ **1**. A typical experimental procedure was as follows: The solid $K_{10}[\alpha_2$-$P_2W_{17}O_{61}]\cdot 10H_2O$ (3 g, 0.6

mmol) and an excess of $(CH_3O)_3SiC_6H_4CH_2Cl$ (444 mg, 1.8 mmol) were added into component solvent CH_3CN/H_2O (60 ml / 30 ml). Then the pH of the mixture was fixed at 2 to get a clear yellow solution. The solution was stirred for 6 hours at room temperature. Then CH_3CN was partially evaporated and the residue solvent was added into an aqueous solution of NBu_4Br (3 g, 9.3 mmol in 30 ml H_2O) to precipitate the expected product as NBu_4 ammonium salt. The product was filtered, washed with water and ethanol, and dried with diethylether. (Yield: 2.9 g (0.48 mmol, 80%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.74 (*d*, *J* = 7.8 Hz, 4H, H-arom), 7.42 (*d*, *J* = 7.9 Hz, 4H, H-arom), 4.75 (*s*, 4H, CH_2–Cl), 3.34 - 3.06 (*m*, 48H, CH_2-N), 1.57 (*m*, 48H, CH_2–CH_2N), 1.32 (*m*, 48H, CH_2–CH_3), 0.94 (*t*, *J* = 7.3 Hz, 72H, CH_3). ^{31}P NMR (121.5 MHz, DMSO-d_6): δ = –10.3 (s, PW_8), –13.3 (s, PW_9).

Synthesis of $(NBu_4)_6[\alpha_2$-$P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$: 2

Two-azido-containing polyoxometalate (A-POM) (compound **2)** was easily obtained via a simple substitution reaction of compound **1** and sodium azide (NaN_3). Compound **1** (2 g, 0.34 mmol) and NaN_3 (0.22 g, 3.4 mmol) were dissolved in 30 ml DMF, and the undissolved NaN_3 was dissolved by adding a little H_2O. The solution was stirred at 50°C for 24 hours. Then the solvent was evaporated and the product was precipitated in H_2O. The product was filtered, washed with water and ethanol, and dried with diethylether. (Yield: 1.8 g (0.3 mmol, 88%). ^{1}H NMR (400

MHz, DMSO-d_6): δ = 7.76 (*d*, *J* = 7.5 Hz, 4H, H-arom), 7.35 (*d*, *J* = 7.5 Hz, 4H, H-arom), 4.44 (*s*, 4H, CH_2–N_3), 3.29 - 3.09 (*m*, 48H, CH_2–N), 1.57 (*m*, 48H, CH_2–CH_2N), 1.32 (*m*, 48H, CH_2–CH_3), 0.92 (*t*, *J* = 7.3 Hz, 72H, CH_3). ^{31}P NMR (121.5 MHz, DMSO-d_6): δ = –10.3 (s, PW_8), –13.3 (s, PW_9). ESI/MS: see below for full details.

Charge	Simulated m/z	Observed m/z	Aggregates
4	1125.4	1126.9	$H_2[\alpha_2\text{-}P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$
4	1186.2	1187.1	$(NBu_4)H[\alpha_2\text{-}P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$
3	1500.8	1500.5	$H_3[\alpha_2\text{-}P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$
3	1581.2	1581.5	$(NBu_4)H_2[\alpha_2\text{-}P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$
3	1661.7	1662.6	$(NBu_4)_2H[\alpha_2\text{-}P_2W_{17}O_{61}(SiC_6H_4CH_2N_3)_2O]$
3	1742.2	1741.6	$(NBu_4)_3[\alpha_2\text{-}P_2W_{17}O6_1(SiC_6H_4CH_2N_3)_2O]$

Synthesis of PT-PCL by ROP

The propargyl-terminated poly(ε-caprolactone) was synthesized according to the reported procedure.[3] A typical experimental procedure was as follows: The propargyl-terminated PCL was prepared by ROP of ε-CL in toluene with $Sn(Oct)_2$ as a catalyst and propargyl alcohol as an initiator. Propargyl alcohol (65 mg, 1.2 mmol), ε-CL (8.0 g, 70.2 mmol), and 20 ml of toluene were added to a previously dried Schlenk flask. After three freeze-pump-thaw cycles, $Sn(Oct)_2$ (118 mg, 0.29 mmol) was

added under argon. The Schlenk flask was then placed in an oil bath thermostated at 80°C for 16 hours. The polymerization was stopped by cooling to room temperature and opening the flask to air. The mixture was precipitated into an excess methanol, filtered off, and dried at room temperature in a vacuum. $\overline{M}_{n,GPC}$ = 7.7×10^3, $\overline{M}_w/\overline{M}_n$ = 1.13. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.67 (*d*, *J* = 2.4 Hz, 2H, –O–CH_2–CCH), 3.98 (*t*, *J* = 6.5 Hz, 76H, CH_2–OC=O), 2.27 (*t*, *J* = 7.3 Hz, 76H, CH_2–C=O), 1.64 - 1.47 (*m*, 152H, CH_2–CH_2C=O, CH_2–CH_2O), 1.36 - 1.23 (*m*, 76H, CH_2–CH_2CH_2O–).

General procedure for the synthesis of hybrid polymers

1 equivalent of A-POM **2**, 2.2 equivalents of PT-PCL and 15 ml DMF were added to a 50 mL Schlenk flask equipped with a stir bar. The contents were stirred to dissolve the A-POM and PT-PCL.. Under argon, 2 equivalents of $CuSO_4$•$5H_2O$ and 4 equivalents of ascorbic acid were added to form a mixture because $CuSO_4$•$5H_2O$ did not fully dissolve in DMF. The reaction was then conducted at room temperature for PT-PCL-20 and PT-PCL-38 or 50 °C for PT-PCL-102. The reaction was stopped after 8 hours for PT-PCL-20, 16 hours for PT-PCL-38 hours and 24 hours for PT-PCL-102. The flocculent precipitate in resulting reaction mixture was then separated by centrifugation. The obtained filtrate was treated with TBA^+ ion-treated cation-exchange resin (Dowex 50W X2, 100-200 mesh) for 12h. Then the clear filtrate was concentrated and

precipitated into an excess methanol. The precipitate was filtered off and dried at room temperature in a vacuum. The pure PCL-POM-PCL hybrids were obtained by subsequent fractional precipitation with THF/MeOH. The crude precipitates were redissolved in THF in a concentration of 0.015 (g/ml) for PCL-POM-PCL-20 and 0.010 (g/ml) for PCL-POM-PCL-38 and 0.005 (g/ml) for PCL-POM-PCL-102. Then methanol was added into these solutions. When about 8 times volume methanol for PCL-POM-PCL-20, 3.5 times volume methanol for PCL-POM-PCL-38 and 0.8 times volume methanol for PCL-POM-PCL-102 were added into the solutions, some floccules appeared. The flocculent precipitate and the filtrate were separated by centrifugation. The separated precipitates were dried under vacuum. The clear filtrate was re-concentrated. A small amount of hybrid polymers existing in the filtrates were obtained using the same fractional precipitation process in order to increase the yield.

PCL-POM-PCL-20 (58%) : ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.24 (*s*, 2H, $H_{triazole}$), 7.74 (*s*, 4H, H-arom), 7.29 (*s*, 4H, H-arom), 5.59 (*s*, 4H, CH_2-arom), 5.08 (*s*, 4H, CH_2-triazole), 3.98 (*t*, *J* = 6.3Hz, 80H, CH_2–OC=O), 3.17 (*m*, 21H, CH_2–N), 2.27 (*t*, *J* = 7.1Hz, 80H, CH_2–C=O), 1.54 (*m*, 180H, CH_2–CH_2C=O, CH_2–CH_2O–, CH_2–CH_2N), 1.30 (*m*, 100H, CH_2–CH_2CH_2O–, CH_2–CH_3), 0.94 (*t*, *J* = 7.3Hz, 32H, CH_3). ^{31}P NMR (121.5 MHz, DMSO-d_6): δ = –10.3 (s, PW_8), –13.2 (s, PW_9).

PCL-POM-PCL-38 (54%) : ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.21 (*s*, 2H, $H_{triazole}$), 7.74 (*s*, 4H, H-arom), 7.29 (*s*, 4H, H-arom), 5.58 (s, 4H, CH_2-arom), 5.08 (*s*, 4H, CH_2-triazole), 3.98 (*t*, *J* = 6.3Hz, 152H, CH_2–OC=O), 3.17 (*m*, 19H, CH_2-N), 2.27 (*t*, *J* = 7.1Hz, 152H, CH_2–C=O), 1.54 (*m*, 323H, CH_2–CH_2C=O, CH_2–CH_2O–, CH_2–CH_2N), 1.30 (*m*, 171H, CH_2–CH_2CH_2O–, CH_2–CH_3), 0.94 (t, *J* = 7.2Hz, 30H, CH_3). ^{31}P NMR (121.5 MHz, DMSO-d_6): δ = −10.3 (s, PW_8), −13.3 (s, PW_9).

PCL-POM-PCL-102 (42%) : ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.16 (*s*, 2H, $H_{triazole}$), 7.74 (*s*, 4H, H-arom), 7.28 (*s*, 4H, H-arom), 5.58 (*s*, 4H, CH_2-arom), 5.07 (*s*, 4H, CH_2-triazole), 3.98 (*t*, *J* = 6.3Hz, 408H, CH_2–OC=O), 3.16 (*m*, 24H, CH_2–N), 2.27 (*t*, *J* = 7.1Hz, 400H, CH_2–C=O), 1.54 (*m*, 800H, CH_2–CH_2C=O, CH_2–CH_2O–, CH_2–CH_2N), 1.30 (*m*, 422H, CH_2–CH_2CH_2O–, CH_2–CH_3), 0.94 (*t*, *J* = 7.3Hz, 40H, CH_3). ^{31}P NMR (121.5 MHz, DMSO-d_6): δ = −10.3 (s, PW_8), −13.3 (s, PW_9).

References:

(1) R. Contant, *Inorg. Synth.*, 1990, **27**, 104–111.

(2) F. Odobel, M. Séverac, Y. Pellegrin, E. Blart, C. Fosse, C. Cannizzo, C. R. Mayer, K. J. Elliott and A. Harriman, *Chem. Eur. J.*, 2009, **15**, 3130–3138.

(3) X. H. He, L. Y. Liang, M. R. Xie, Y. Q. Zhang, S. L. Lin and D. Y. Yan, *Macromol. Chem. Phys.*, 2007, **208**, 1797–1802.

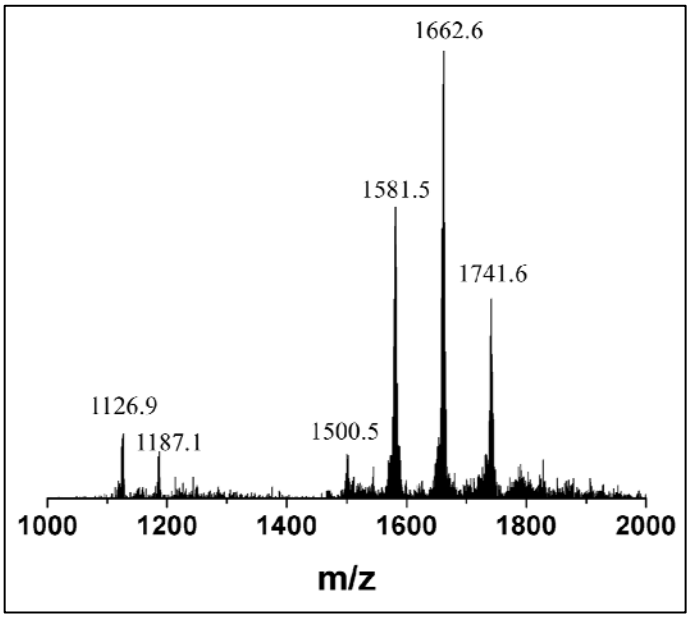

Figure S1. ESI-MS spectrum of A-POM **2**.

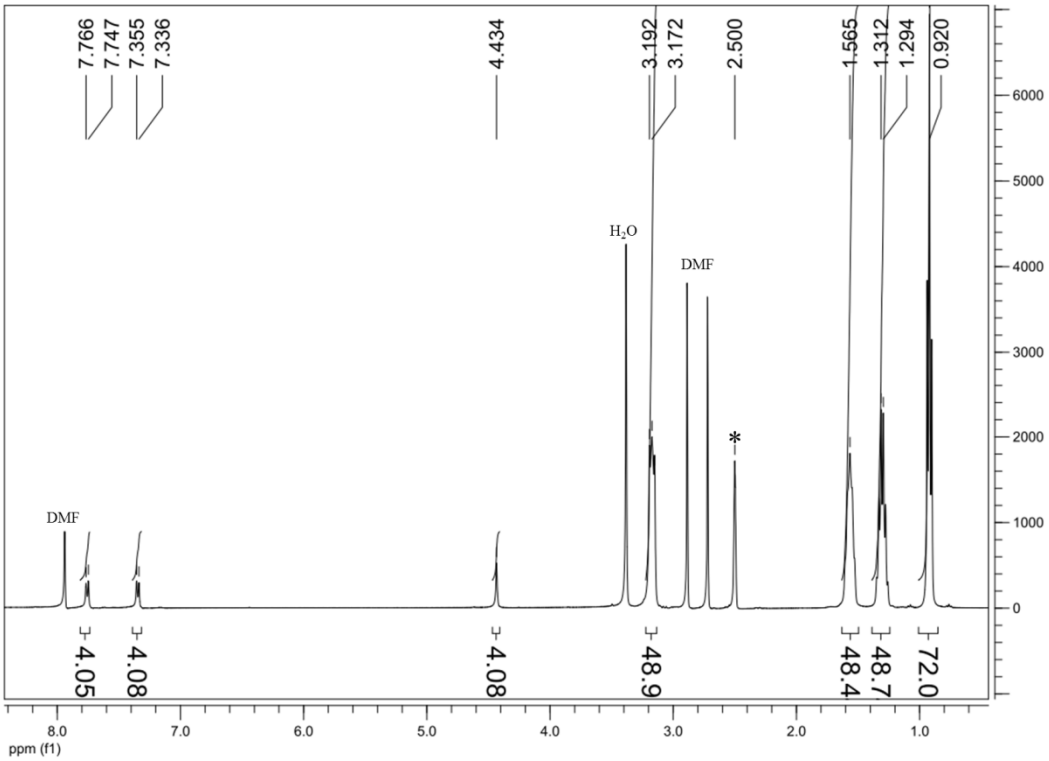

Figure S2. ^{1}H NMR spectrum of A-POM **2**

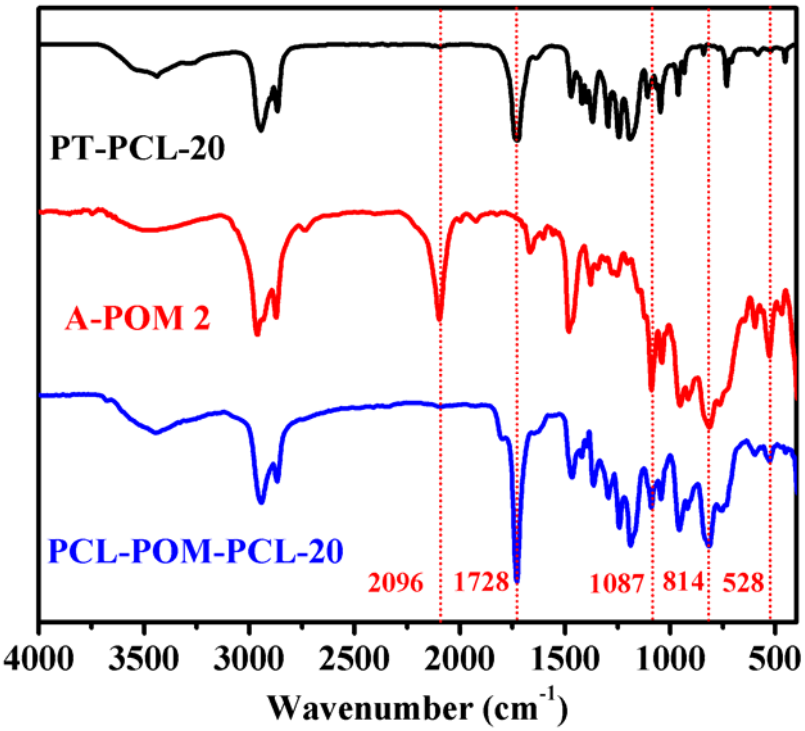

Figure S3. FT-IR spectrum of PCL-POM-PCL-20.

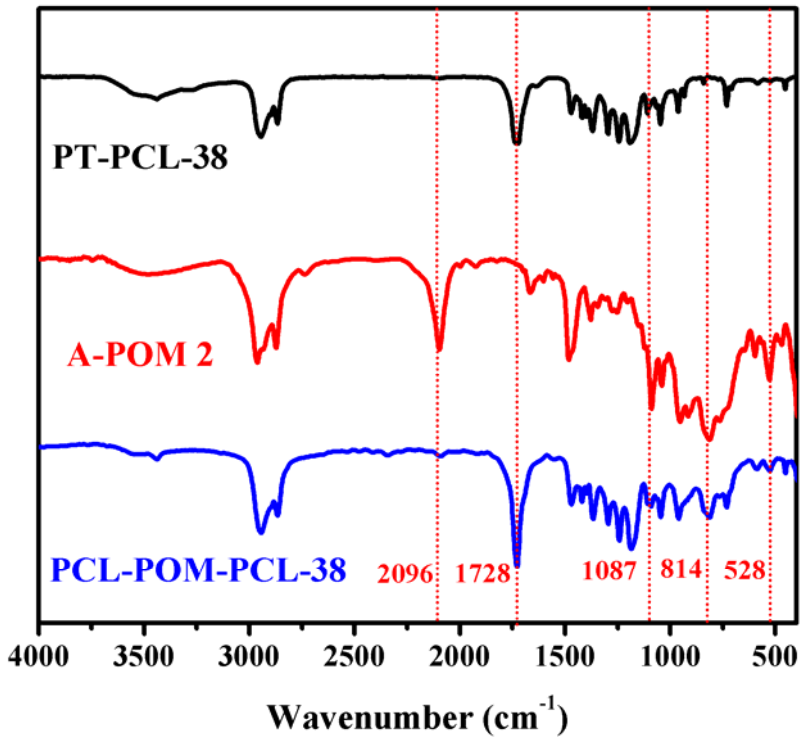

Figure S4. FT-IR spectrum of PCL-POM-PCL-38.

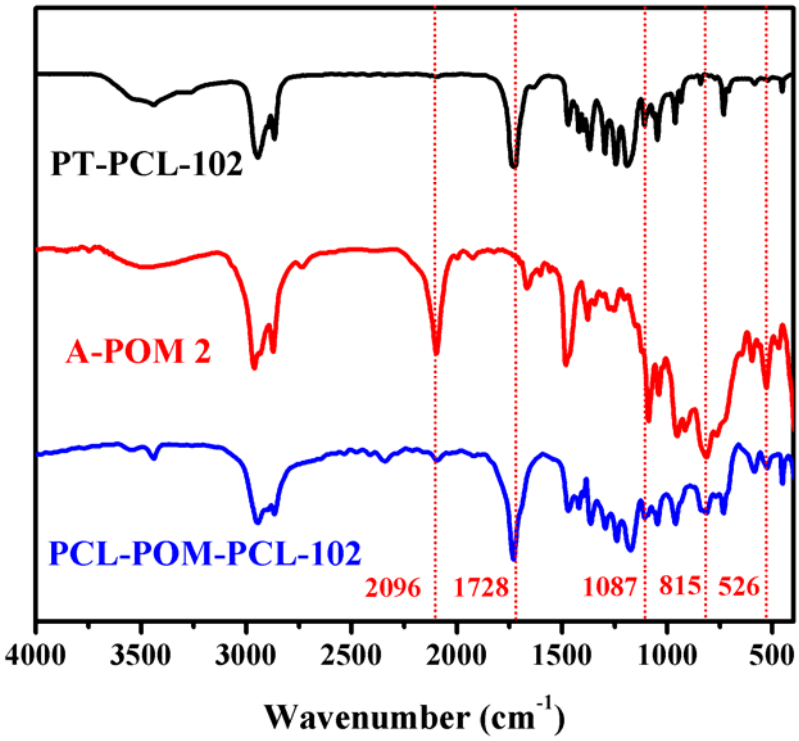

Figure S5. FT-IR spectrum of PCL-POM-PCL-102.

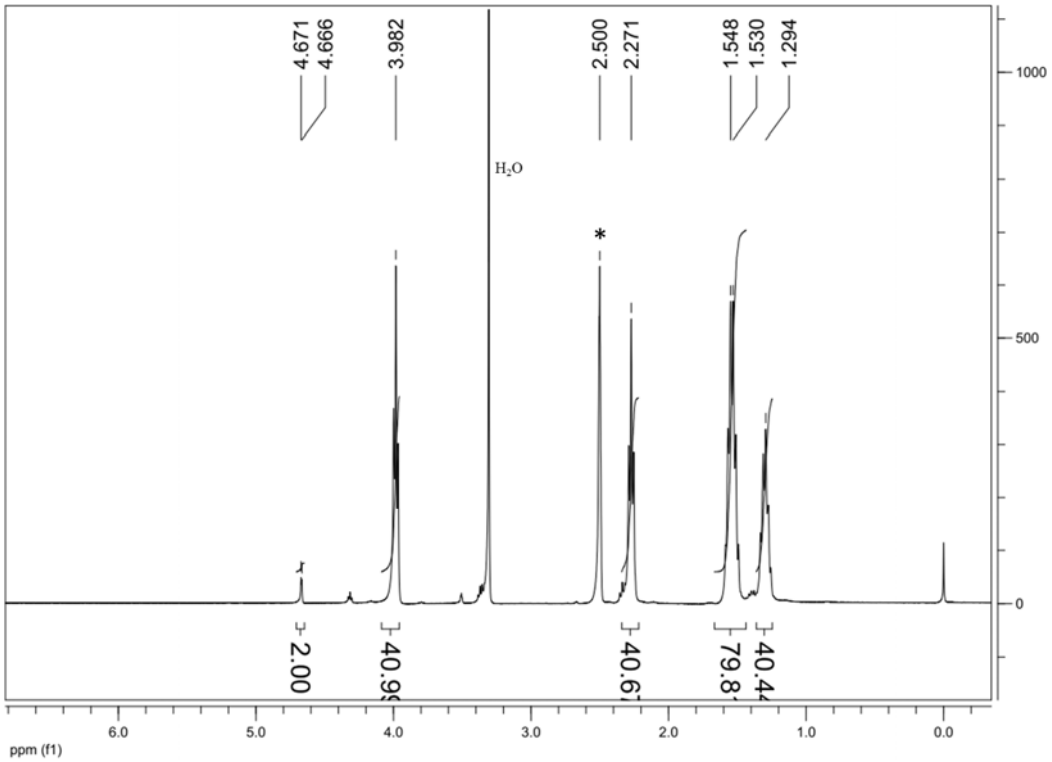

Figure S6. ^{1}H NMR spectrum of PT-PCL-20.

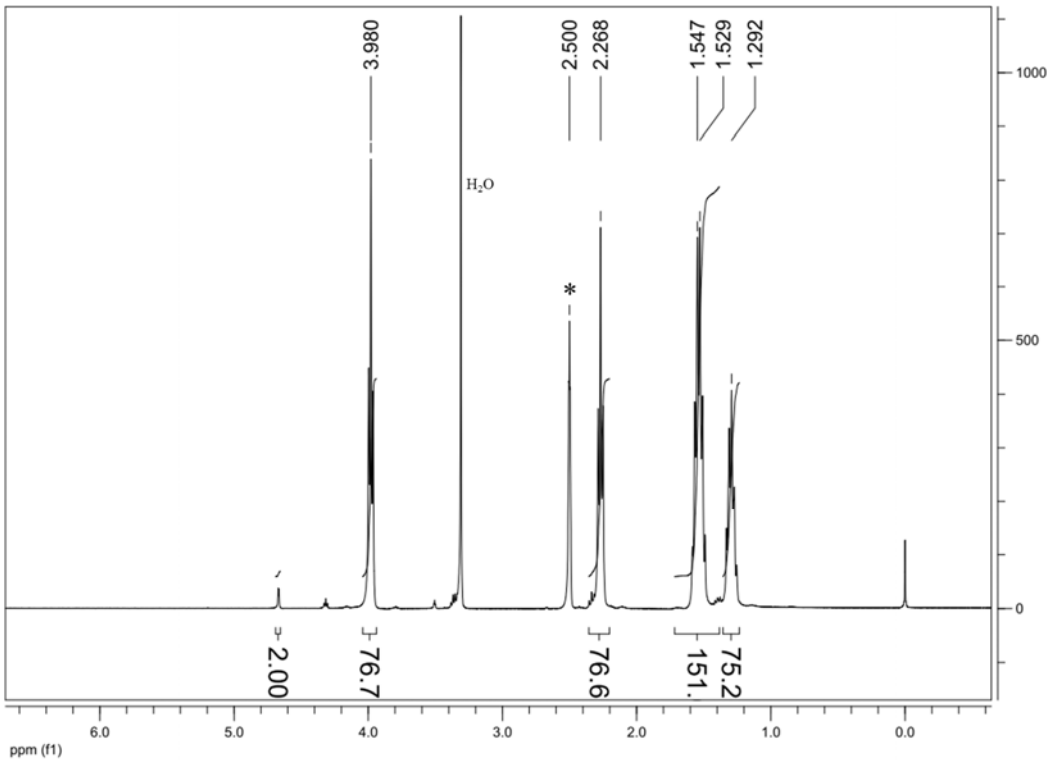

Figure S7. ^{1}H NMR spectrum of PT-PCL-38.

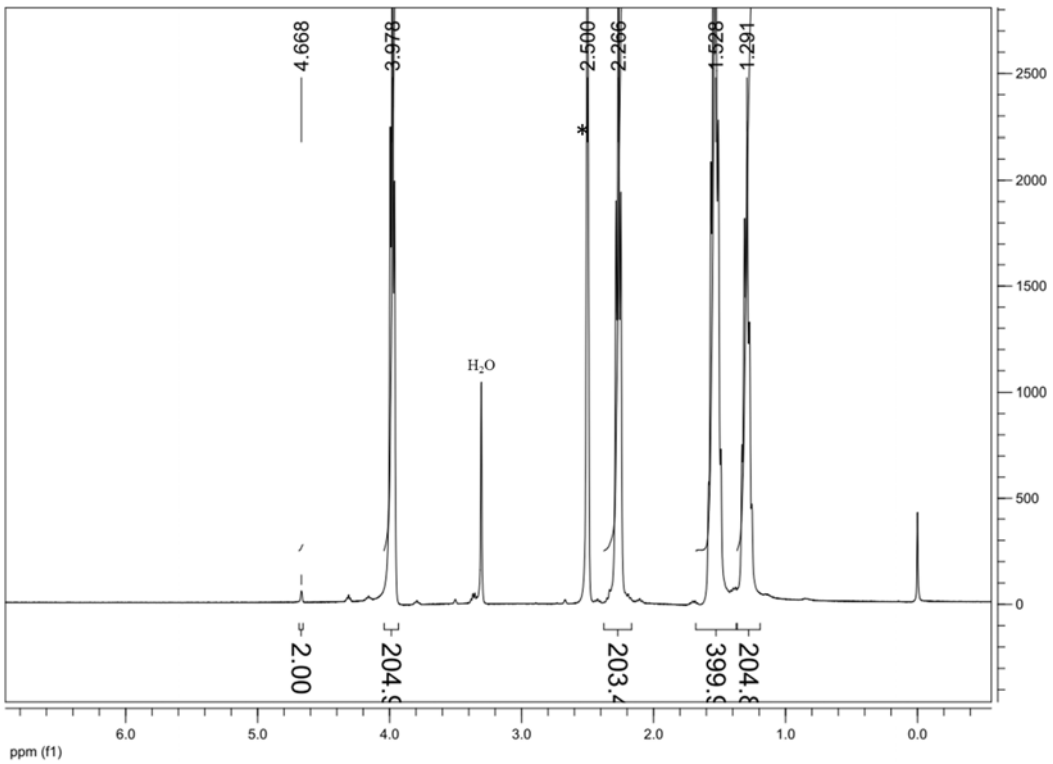

Figure S8. ^{1}H NMR spectrum of PT-PCL-102.

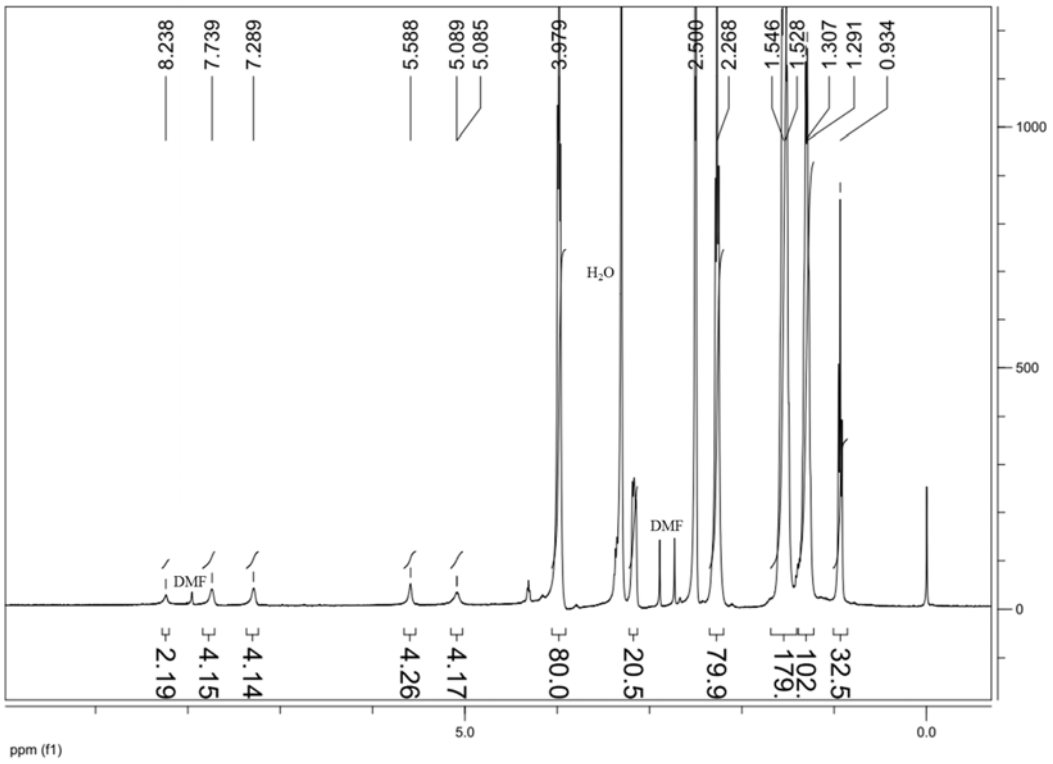

Figure S9. ^{1}H NMR spectrum of PCL-POM-PCL-20.

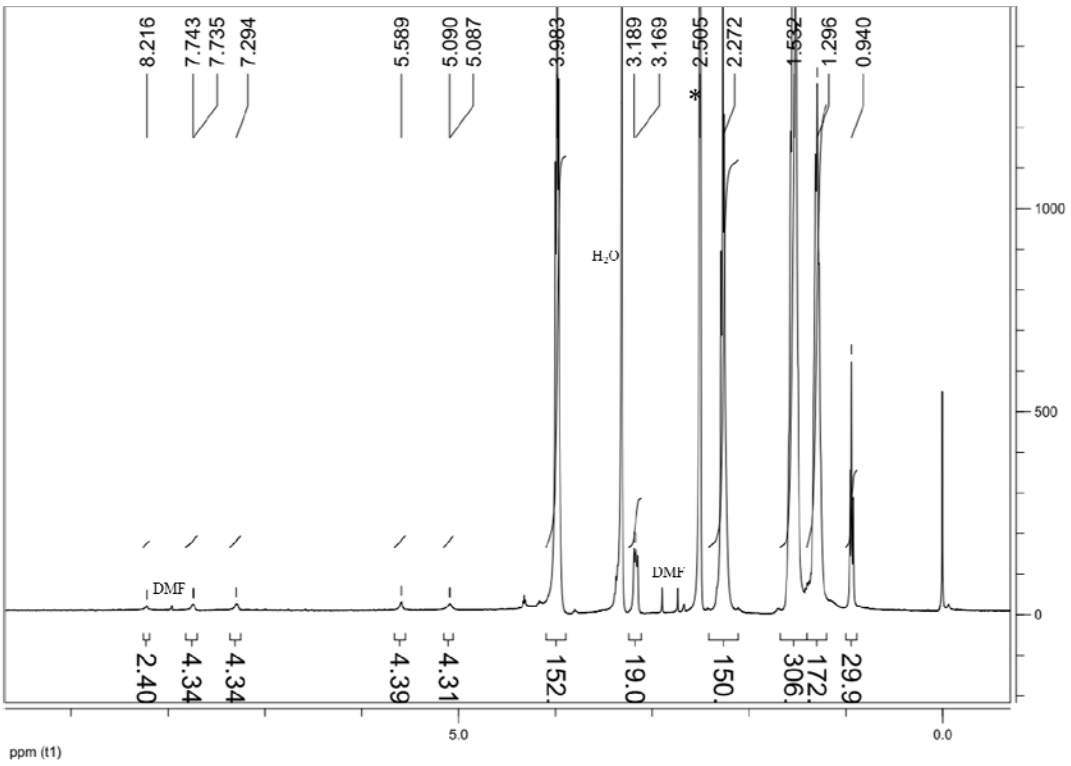

Figure S10. ^{1}H NMR spectrum of PCL-POM-PCL-38.

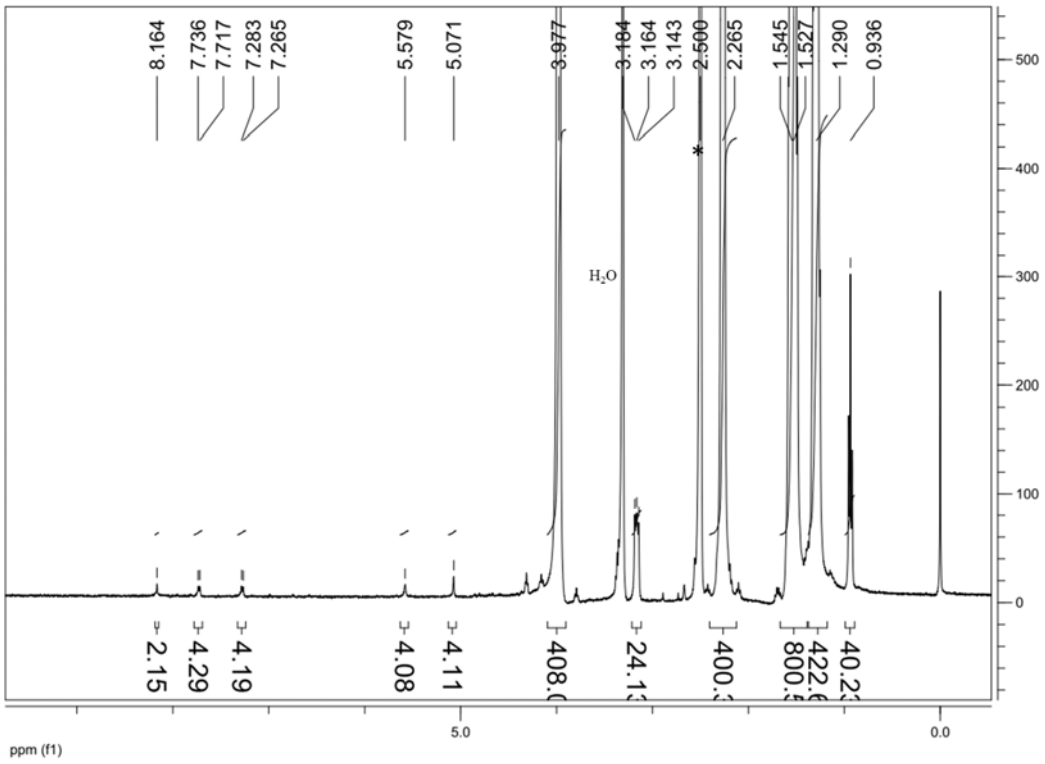

Figure S11. ^{1}H NMR spectrum of PCL-POM-PCL-102.

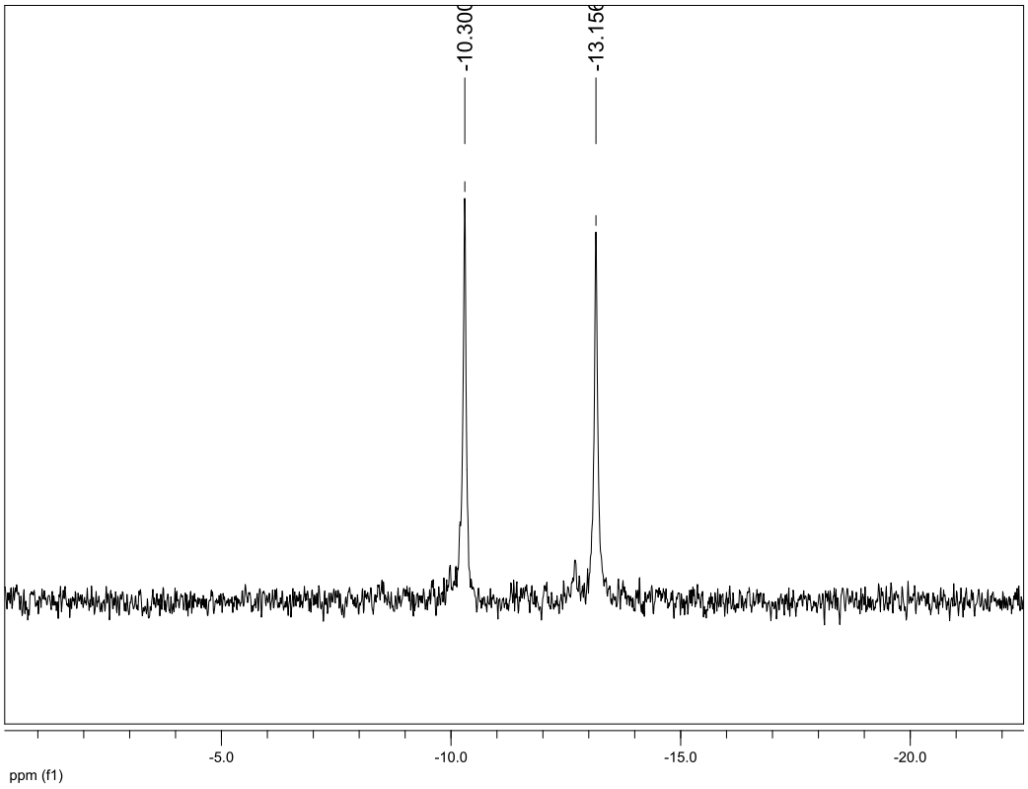

Figure S12. ^{31}P NMR spectrum of PCL-POM-PCL-20.

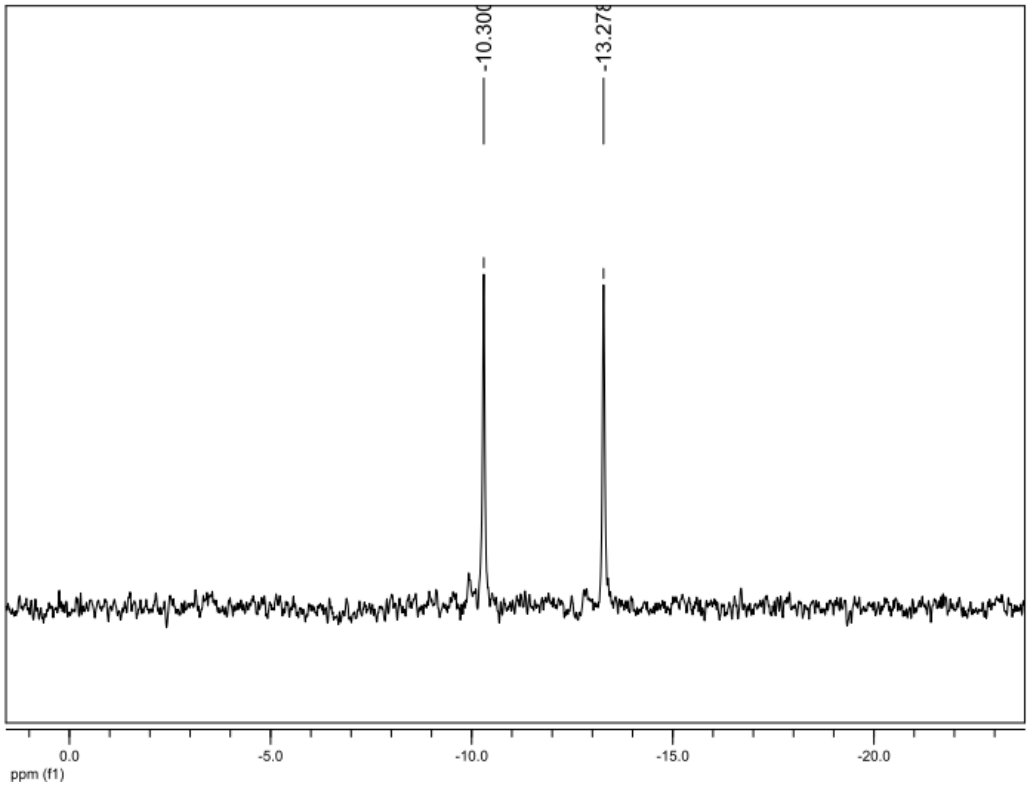

Figure S13. ^{31}P NMR spectrum of PCL-POM-PCL38.

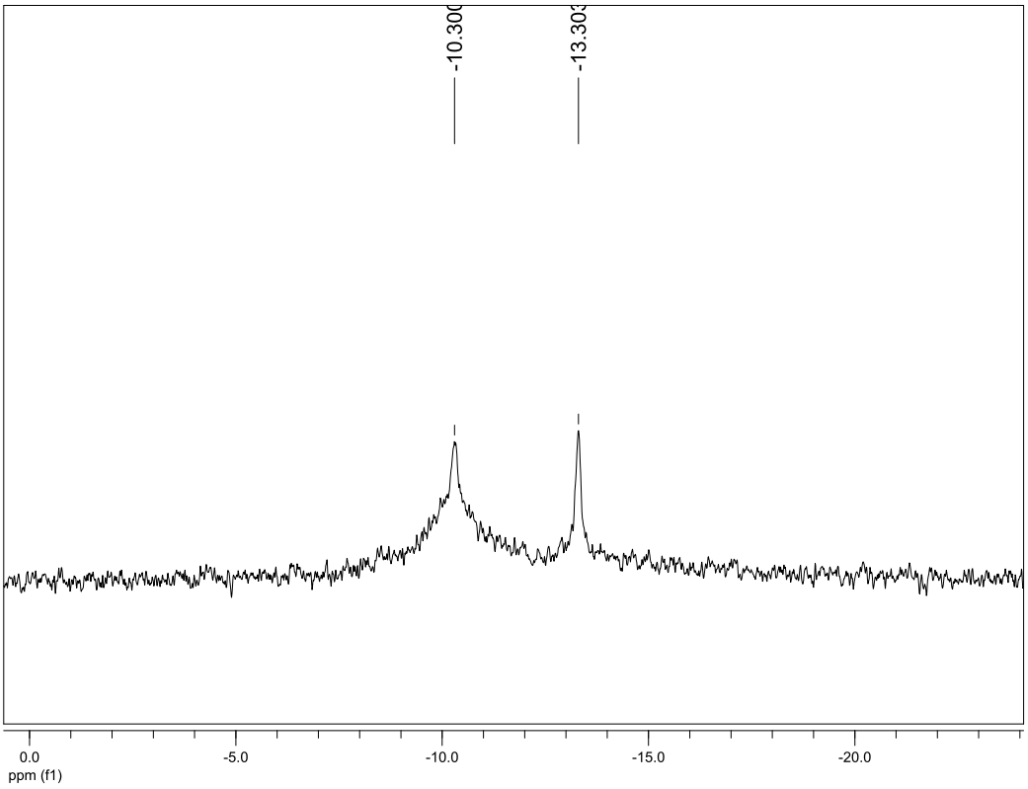

Figure S14. ^{31}P NMR spectrum of PCL-POM-PCL-102.

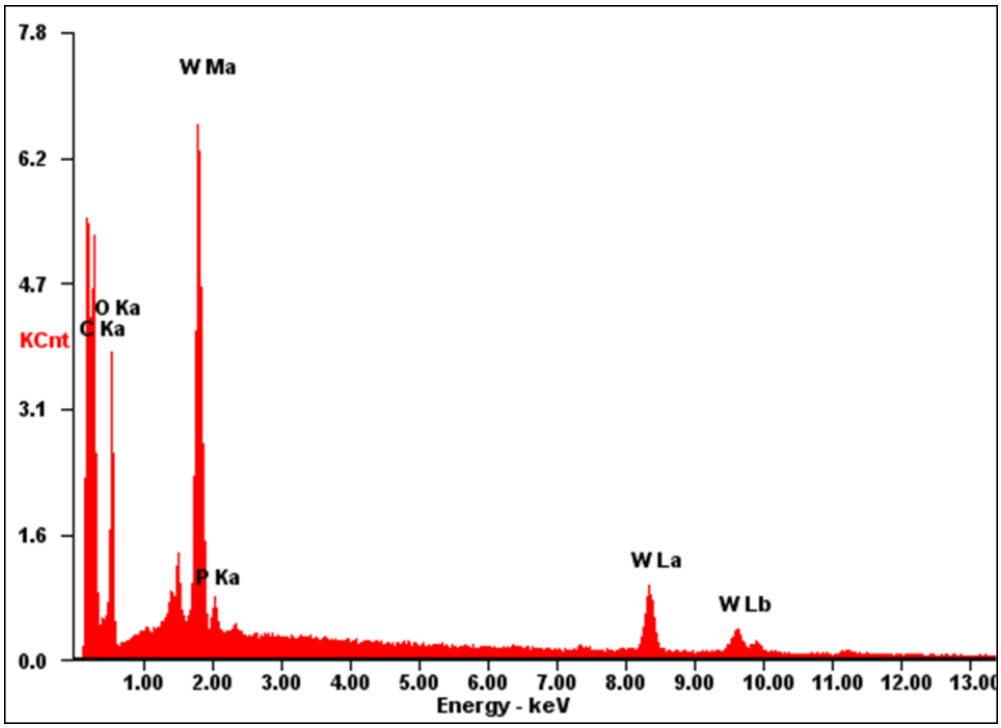

Figure S15. EDX spectrum of the PCL-POM-PCL-20 hybrid showing a K peak of phosphorus and M and L peaks of tungsten.

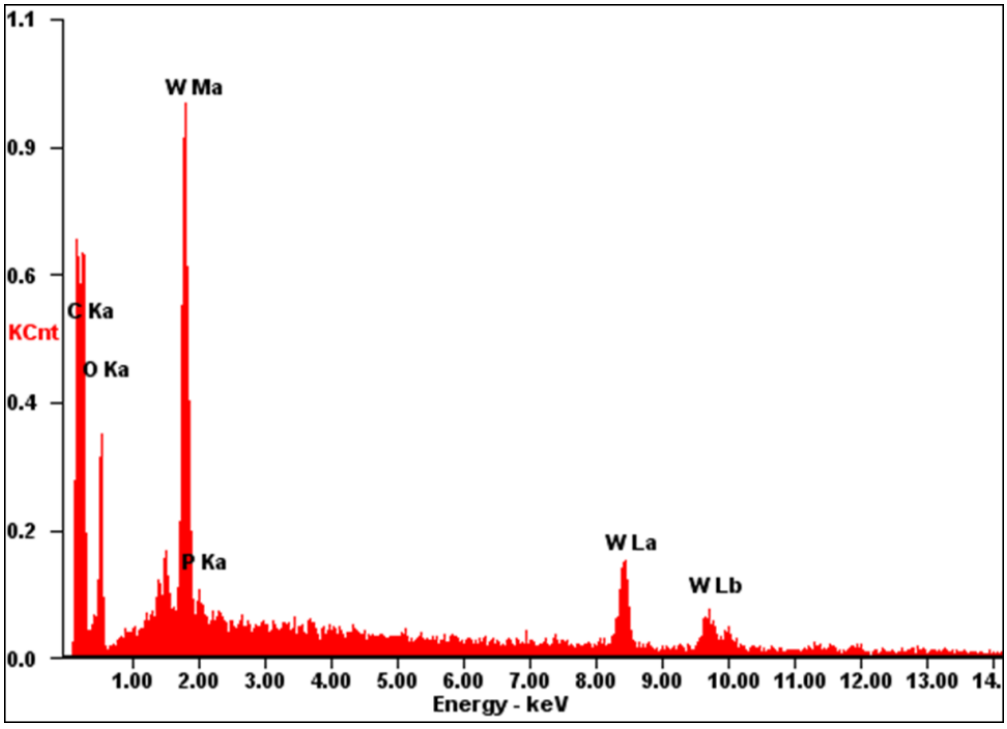

Figure S16. EDX spectrum of the PCL-POM-PCL-38 hybrid showing a K peak of phosphorus and M and L peaks of tungsten.

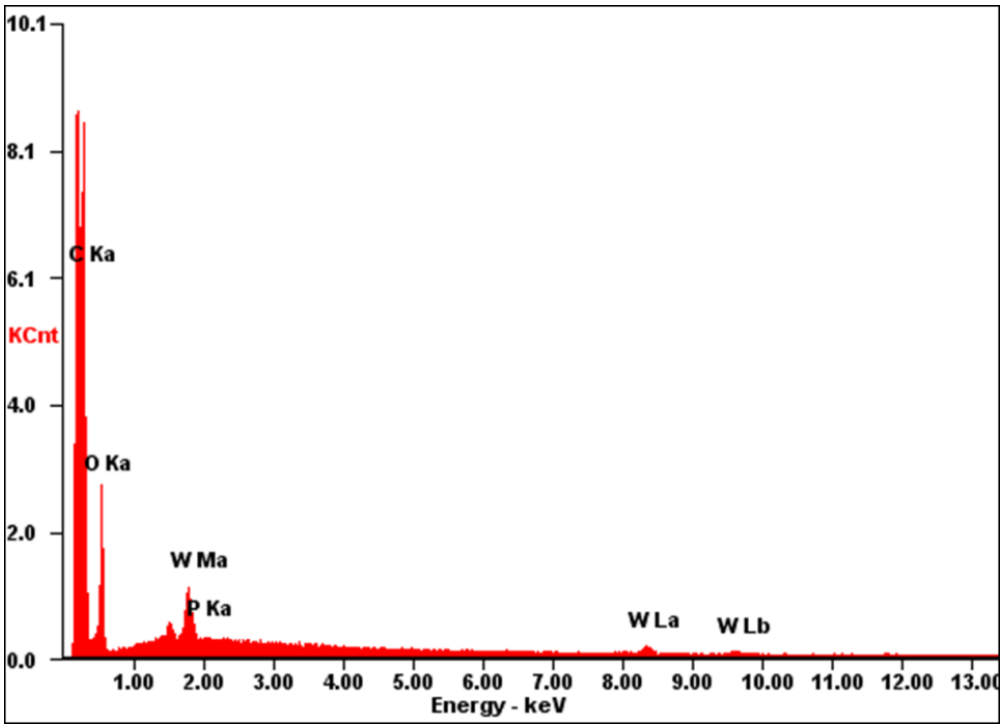

Figure S17. EDX spectrum of the PCL-POM-PCL-102 hybrid showing a K peak of phosphorus and M and L peaks of tungsten.

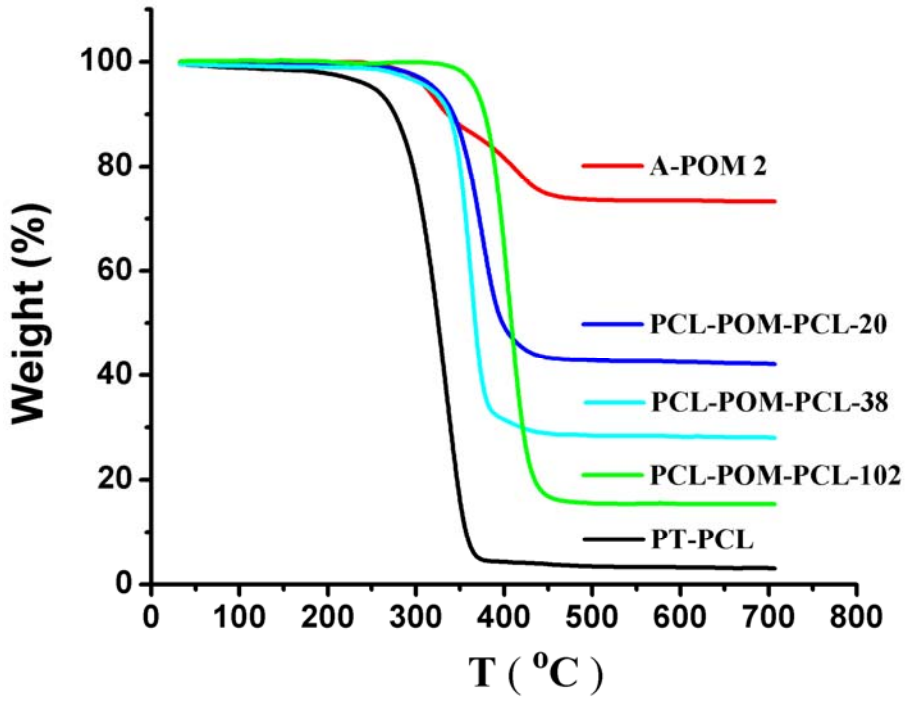

Figure S18. TGA thermograms of A-POM 2, PT-PCL and PCL-POM-PCL hybrids.

Table S1. TGA results of PCL-POM-PCL hybrids

samples	Calculated [a]	Observed
PCL-POM-PCL-20	41.1%	42.1%
PCL-POM-PCL-38	31.4%	28.1%
PCL-POM-PCL-102	17.3%	15.3%

[a] The calculated values were obtained via the following formula:

$Wight(\%) = (73.3\% M_{A-POM\,2} + 3.1\% M_{PT-PCL}) / (M_{A-POM\,2} + 2M_{PT-PCL})$, where 73.3% and 3.1% meant the residues of A-POM **2** and PT-PCL precursors which obtained from the TGA thermograms.