Supplemental Information
for

Intra-chain radical chemistry as a route to poly(norbornene imide) single-chain nanoparticles: structural considerations and the role of adventitious oxygen.

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Supporting Information

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I. Supporting Figures

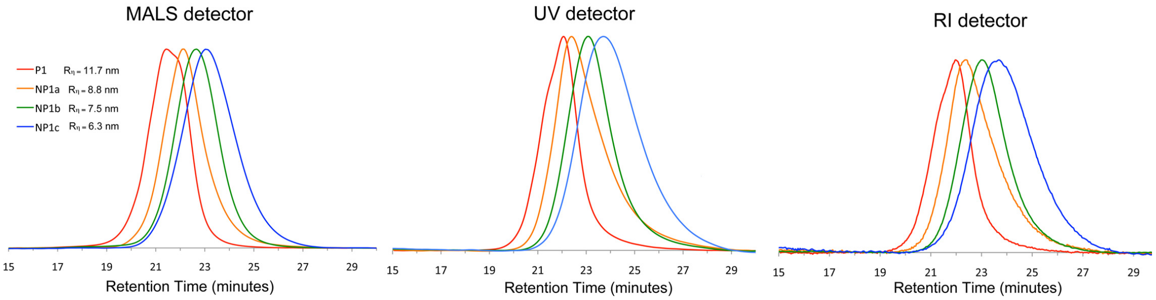


Figure S1: SEC MALS, UV and RI detector traces for P1 and an NP1a-c

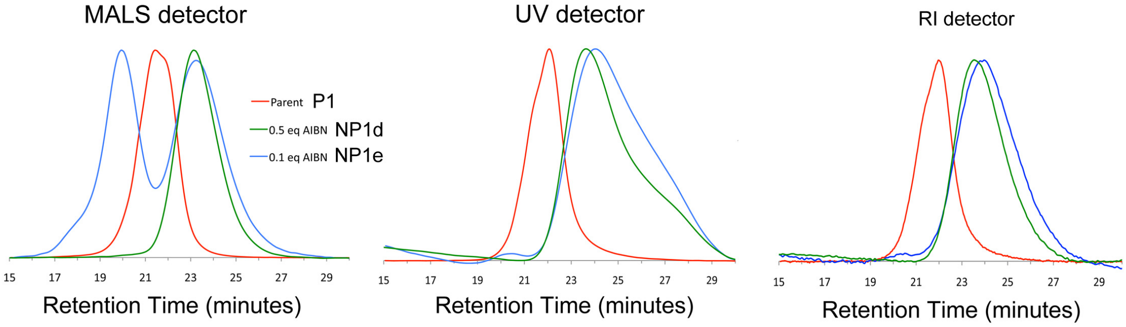


Figure S2: SEC MALS, UV, and RI detector traces for NP1d and NP1e (P1 shown for comparison)

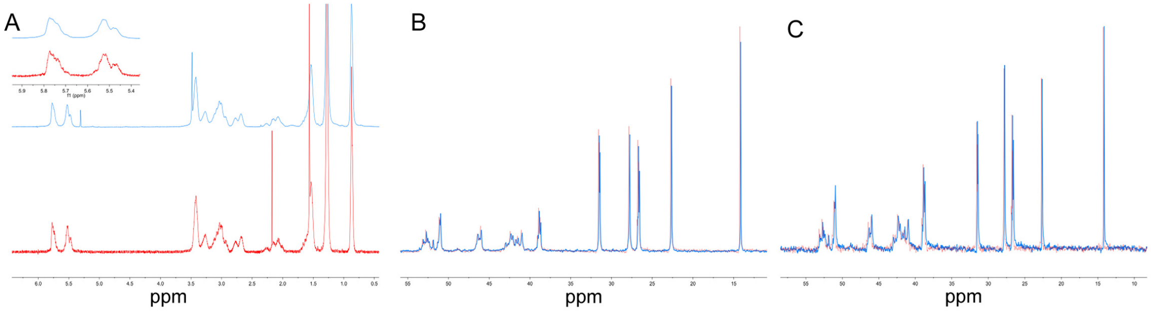


Figure S3: (A) overlay of P2 (top) and NP2 (bottom) ^{1}H NMR spectra highlighting the retention of olefin signals after cross-linking. (B) ^{13}C NMR and (C) ^{13}C DEPT NMR spectra overlay for P2 (red) and NP2 (blue) showing slight shifts in carbon signals before and after cross-linking.

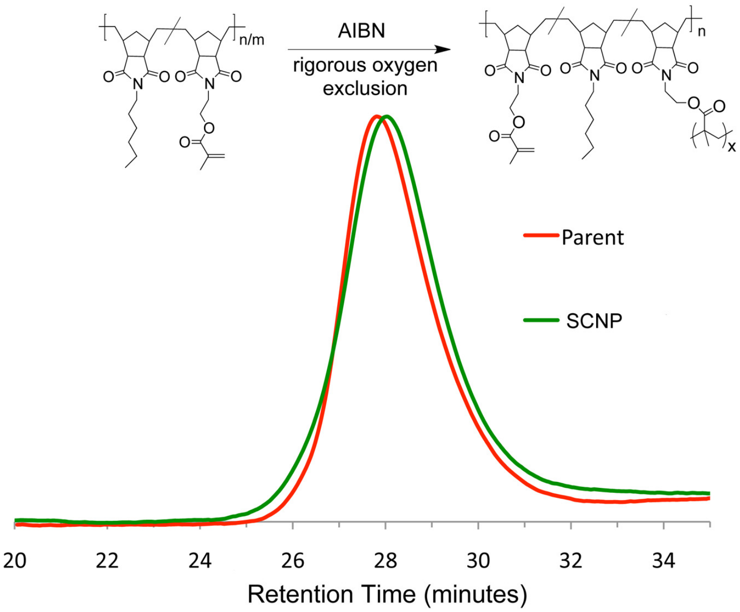


Figure S4: SEC overlay of a P3 before and after intra-chain cross-linking under rigorous oxygen exclusion.

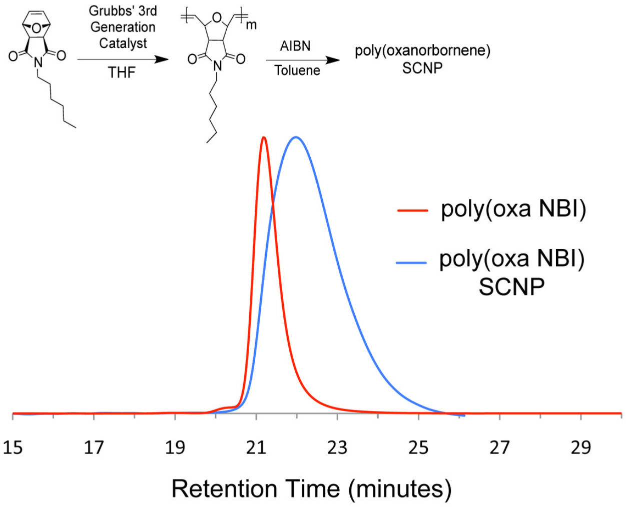


Figure S5: SEC overlay of a poly(oxanorbornene imide) before and after intra-chain cross-linking.

II. Experimental Section

Materials

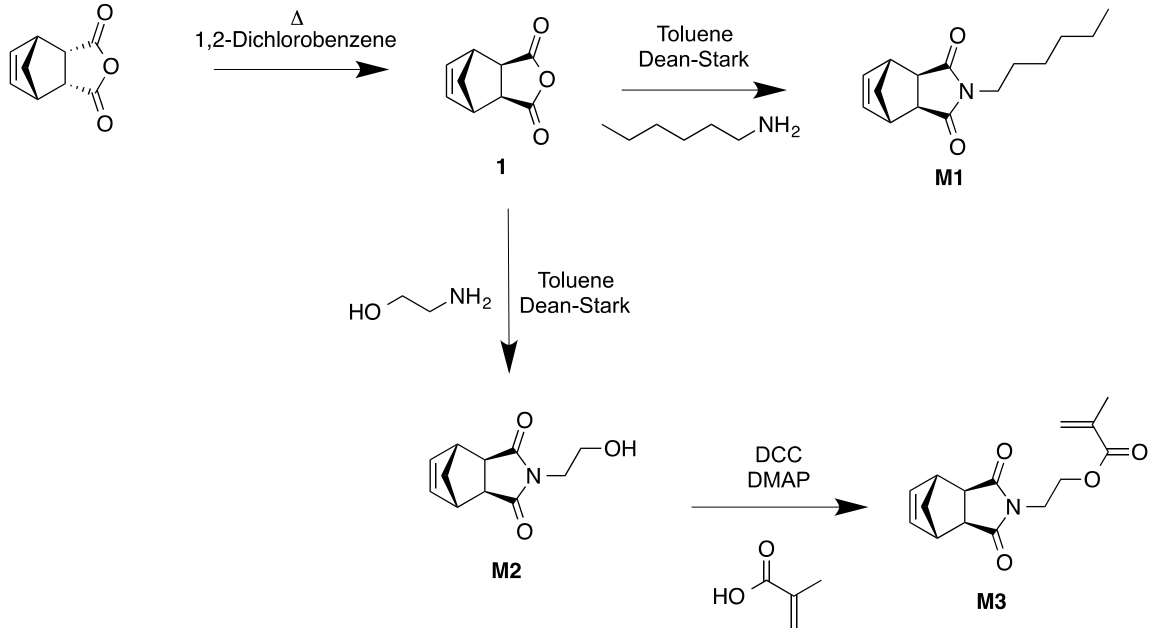
Reagents were obtained from the indicated commercial suppliers and used as received: carbic anhydride (Sigma Aldrich), hexyl amine (Sigma Aldrich), ethanolamine (Sigma Aldrich), methacrylic acid (Sigma Aldrich), N,N'-dicyclohexylcarbodiimide (Sigma Aldrich), dimethyl amino pyridine (Sigma Aldrich), methyl methacrylate (Sigma Aldrich), maleimide (Sigma Aldrich), furan

(Sigma Aldrich), dichloromethane (Fisher Scientific), hexanes (Fisher Scientific), methanol (Fisher Scientific), tetrahydrafuran (Fisher Scientific), silica gel (230-400 mesh) (SiliCycle) Azobisisobutyronitrile (Sigma Aldrich), chloroform-*d* (Cambridge Isotope Laboratories), and 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (Sigma Aldrich). Dry toluene, DCM, and THF were obtained from an Innovative Technology solvent purification system model SPS-400-5.

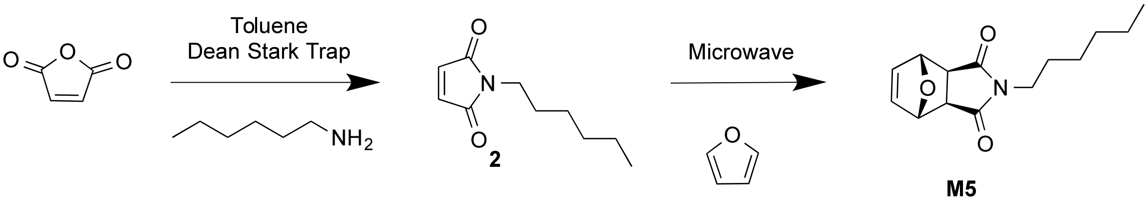
Instrumentation

Photochemical reactions were conducted in a Luzchem photo-reactor CCP-4V equipped with 4 UVA (350 nm centered) and 4 UVC (254 nm centered) lamps. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on a Varian Associates Mercury 400 spectrometer. Solvents ($CDCl_3$) contained 0.03% v/v TMS as an internal reference, chemical shifts (δ) are reported in ppm relative to TMS. Peak abbreviations are used as follows: s=singlet, d=doublet, t=triplet, m=multiplet, br=broad, Ar=Aryl. Size exclusion chromatography (SEC) was performed on a Tosoh EcoSEC dual detection (RI and UV) SEC system coupled to an external Wyatt Technologies miniDAWN Treos multi angle light scattering (MALS) detector and a Wyatt Technologies ViscoStarII differential viscometer. Samples were run in THF at 40 ºC at a flow rate of 0.35 mL/min. The column set was two Tosoh TSKgel SuperMultipore HZ-M columns (4.6x150 mm), one Tosoh TSKgel SuperH3000 column (6x150mm) and one Tosoh TSKgel SuperH4000 column (6x150mm). Increment refractive index values (dn/dc) were calculated online assuming 100% mass recovery (RI as the concentration detector) using the Astra 6 software package (Wyatt Technologies) by selecting the entire trace from analyte peak onset to the onset of the solvent peak or flow marker. This method gave the expected values for polystyrene (dn/dc = .185, Mn = 30k) when applied to a narrow PDI PS standard supplied by Wyatt. Absolute molecular weights and molecular weight distributions were calculated using the Astra 6 software package. Intrinsic viscosity [η] and viscometric hydrodynamic radii (R_h) were calculated from the differential viscometer detector trace and processed using the Astra 6 software.

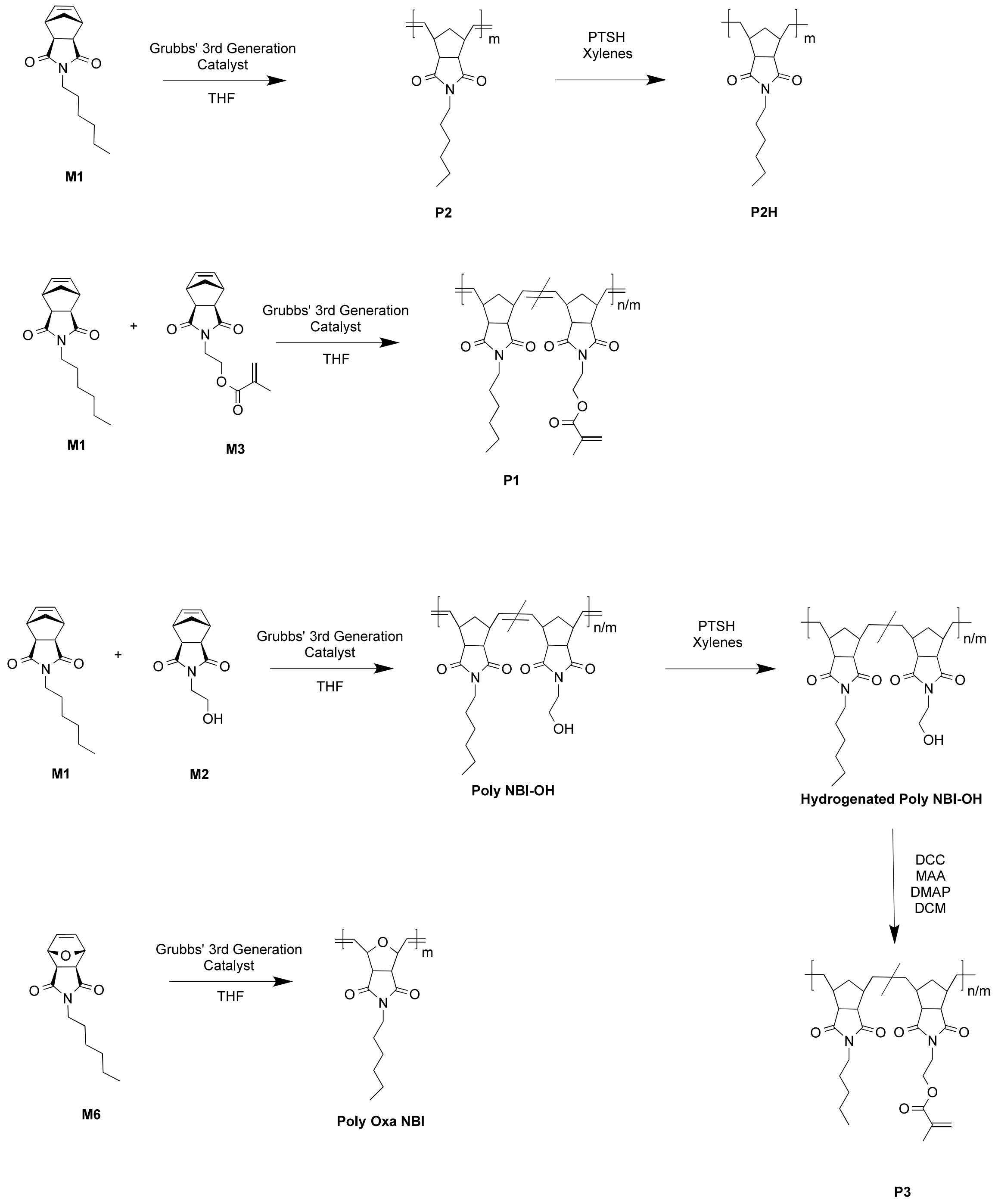
Outline of Synthetic Schemes



Scheme S1 Overview of Norbornene Monomer Synthetic Scheme



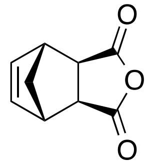
Scheme S2 Overview of Oxanorbornene Synthetic Scheme



Scheme S3 Polymer Synthetic Scheme

Experimental Procedures

Synthesis of Compound 1: 200.16 g of Carbic Anhydride was refluxed in 200 mL of 1,2 dichlorobenzene at 185° C for 4 hours. The solution was then recrystallized from benzene 3x affording approximately 30 g (95% exo) norbornene dicarboximide. ^{1}H NMR (400 MHz $CDCl_3$): δ 6.34 (s, 2H), 3.47 (s, 2H), 3.01 (s, 2H), 1.70-1.67 (m, 1H), 1.48-1.45 (m, 1H)



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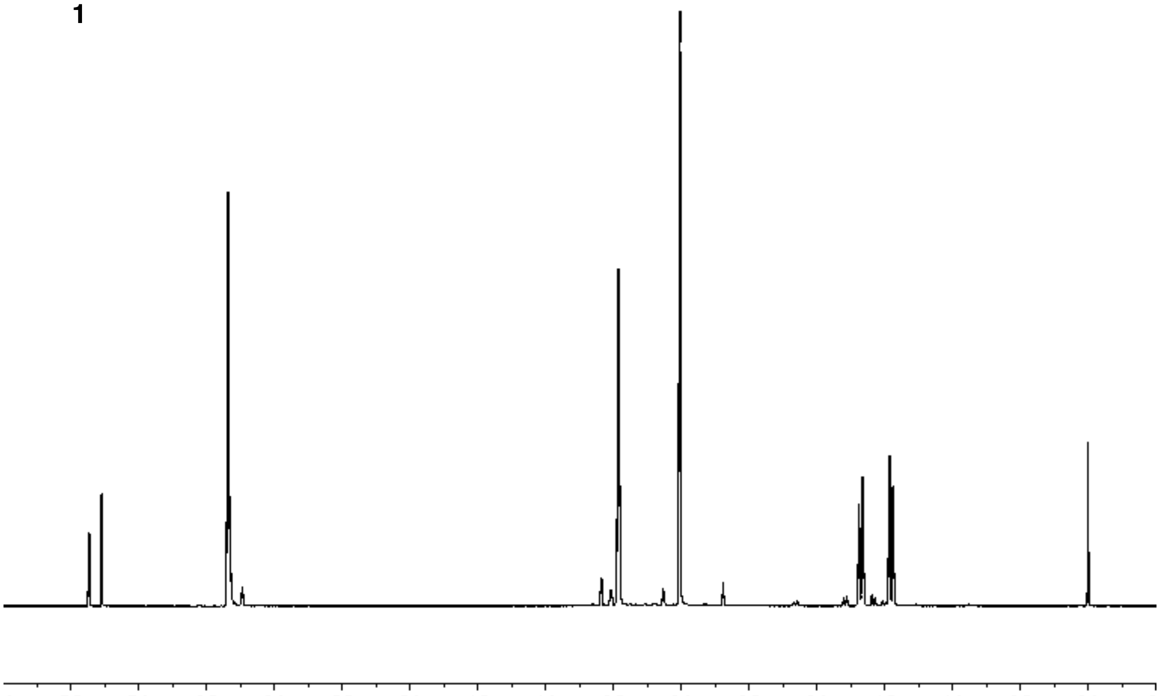


Figure S6 ^{1}H NMR of Exo Carbic Anhydride

Synthesis of M1: Cis-5-norbornene-exo-2,3-dicarboxylic anhydride (3.000g) was added to RBF with 30mL of Toluene. 2.52 mL of hexylamine and 280 μL of triethylamine were added to reaction mixture. A Dean-Stark trap was set up and mixture was heated at 140° C overnight. After 16 hours TLC was performed and all anhydride had been consumed. Toluene was removed by rotary evaporation. Sample was then dissolved in DCM and washed with 30 mL of 0.1N HCL, then 30 mL of brine. The organic layer was dried with $MgSO_4$ and DCM was removed via rotary evaporation. Yield: 2.58 g (57%) ^{1}H NMR (400 MHz $CDCl_3$): δ 6.29 (t, J=1.87 Hz, 2H), 3.50-3.42 (m, 2H), 3.29-3.26 (m, 2H), 2.67 (d, J=1.36 Hz, 2H), 1.60-1.48 (m, 2H), 1.35-1.20 (m, 8H), 0.92-0.82 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 178.33, 138.04, 48.01, 45.38, 42.92, 38.98, 31.54, 27.95, 26.84, 22.69, 14.21.

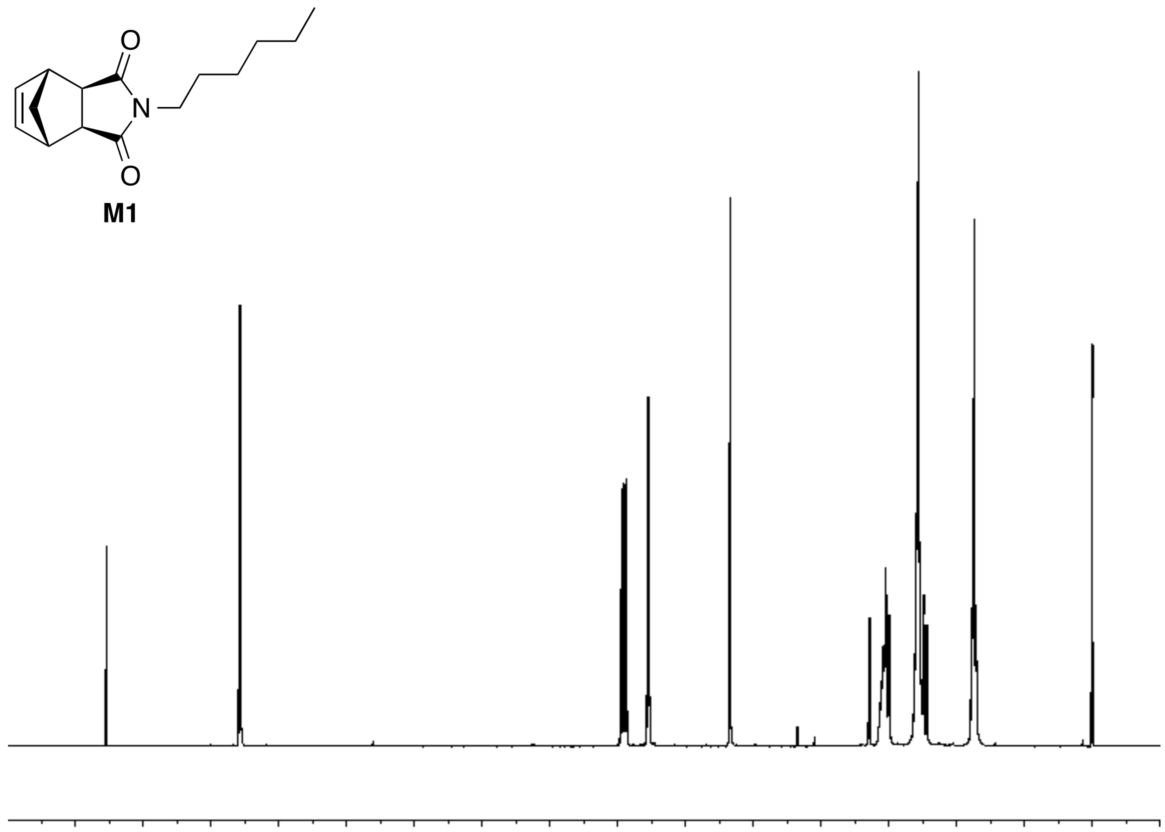


Figure S7 ^{1}H NMR of M1

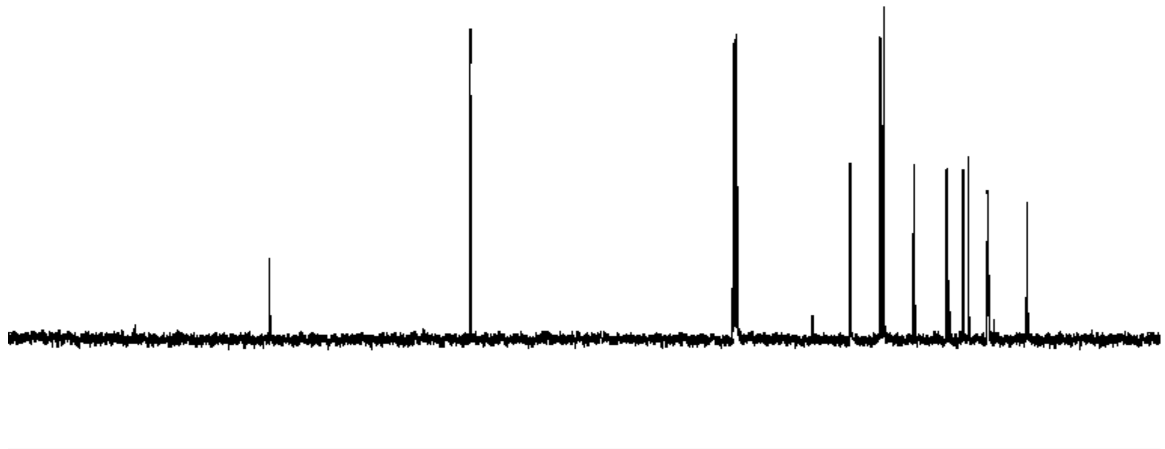


Figure S8 ^{13}C NMR of M1

Synthesis of M2: Cis-5-norbornene-exo-2,3-dicarboxylic anhydride (1.000g) was added to RBF with 10mL of Toluene. 386 μL of 2-aminoethanol and 93 μL of triethylamine were added to reaction mixture. A Dean-Stark trap was set up and mixture was heated at 145° C overnight. After 16 hours TLC was performed and all anhydride had been consumed. Toluene was removed by rotary evaporation. Sample was then dissolved in DCM and washed with 10 mL of 0.1N HCL, then 10 mL of brine. The organic layer was dried with $MgSO_4$ and DCM was removed via rotary evaporation. Yield: 0.987 g (78.27%). ^{1}H NMR (400 MHz $CDCl_3$): δ 6.31 (t, J=1.78 Hz, 2H), 3.82-3.69 (m, 4H), 3.30 (s, 2H), 2.73 (s, 2H), 2.07 (td, J=5.73, 0.67 Hz, 1H), 1.56-1.50 (m, 1H), 1.38-1.32 (m, 1H).

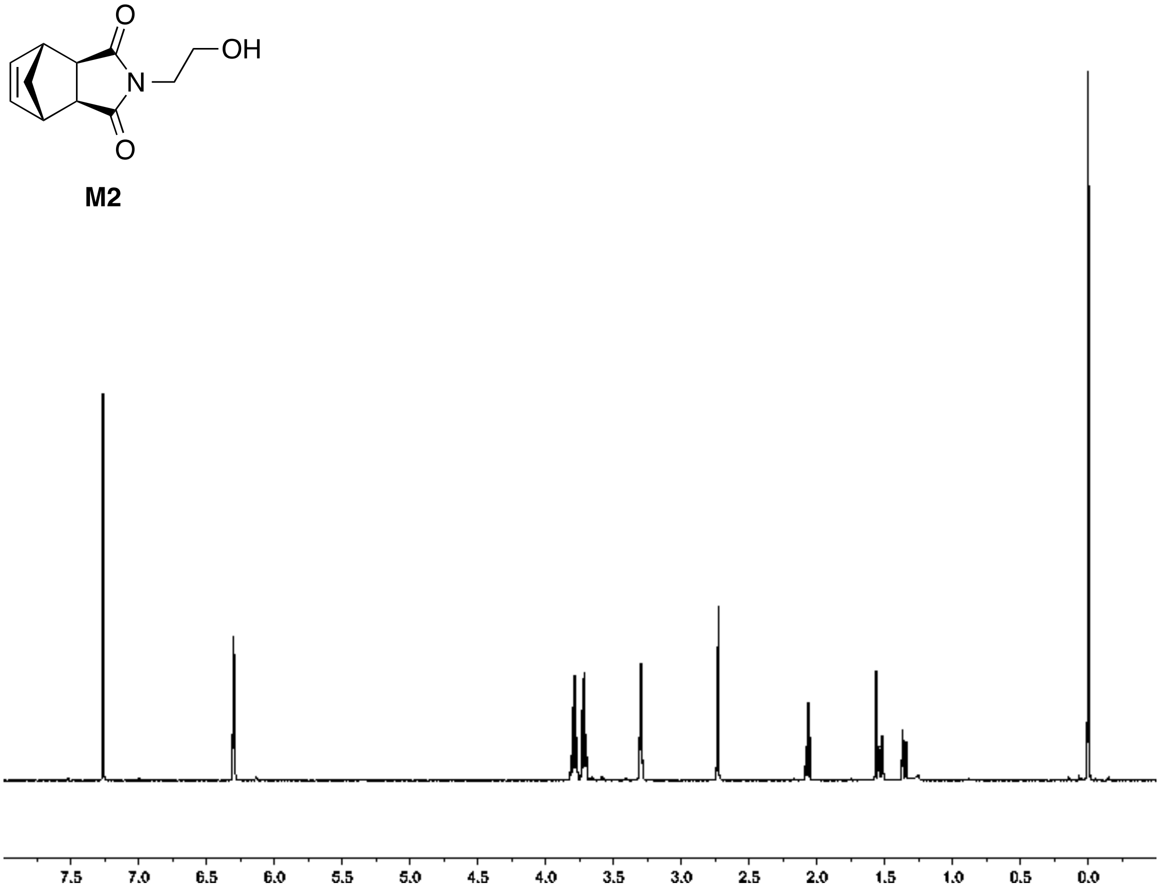


Figure S9 ^{1}H NMR of M2

Synthesis of M3: 1.00g (1 eq) of Exo-N-ethanol-NBI was added to 3 neck RBF. 10 mL of DCM was added and stirred until alcohol dissolved. 1.49 g (1.5 eq) of DCC, 0.0541 g (0.11 eq) of DMAP, and 0.49 mL (1.2 eq) MAA were added to the solution via syringe. Stirred overnight at RT. DCHU was filtered off and solution was washed with DIW (2x20 mL), then dried with $MgSO_4$. DCM was removed by rotary evaporation and product was purified by flash chromatography using gradient of hexanes:EtOAc. Yield: 0.40 g (30%). ^{1}H NMR (400 MHz CDCl$_3$): δ 6.29 (t, J=1.6 Hz, 2H), 6.07-6.04 (m, 1H), 5.57-5.55 (m, 1H), 4.30 (t, J=5.0 Hz, 2H), 3.82 (t, J=5.35 Hz, 2H), 3.29-3.76 (m, 2H), 2.70 (d, J=1.1 Hz, 2H), 1.92-1.87 (m, 4H), 1.30-1.25 (m, 1H). ^{13}C NMR (101 MHz CDCl$_3$): δ 177.98, 167.16, 138.03, 136.01, 126.40, 61.38, 48.04, 45.47, 42.88. 37.70, 18.42.

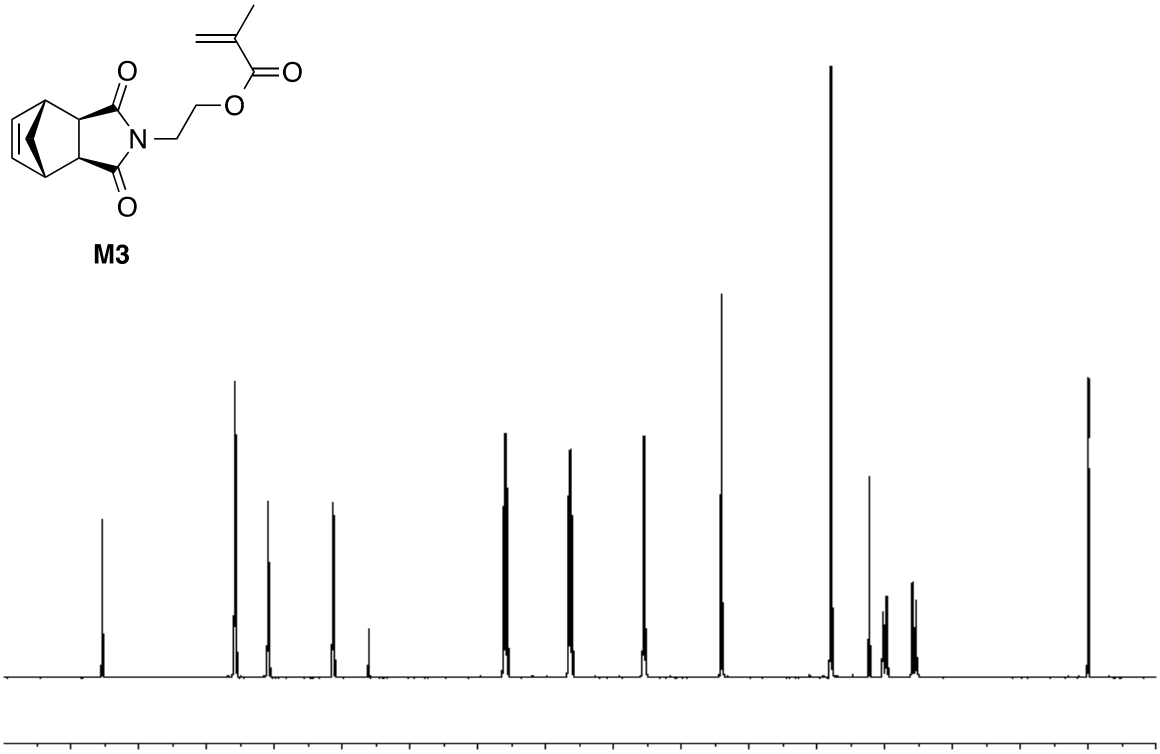


Figure S10 ^{1}H NMR of M3

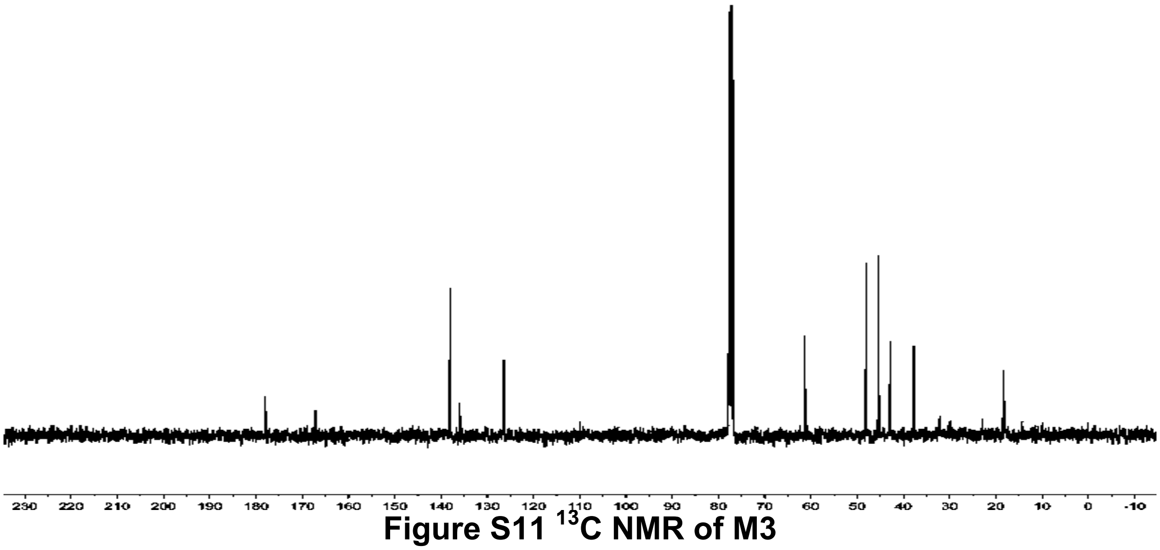


Figure S11 ^{13}C NMR of M3

Synthesis of Compound 2: To a round bottom flask 2.00 g of maleic anhydride and 2.55 mL of hexyl amine were added. 100 mL of toluene and 0.312 mL of triethylamine were added and a Dean-Stark trap was set up. The solution was heated at 140° C overnight. Toluene was removed by rotary evaporation. Sample was then dissolved in DCM and washed with 10 mL of 0.1N HCL, then 10 mL of brine. The organic layer was dried with $MgSO_4$ and DCM was removed via rotary evaporation. Yield 1.95 g (52.78%). ^1H NMR (400 MHz $CDCl_3$): δ 6.68 (s, 2H), 3.60-3.42 (m, 2H), 1.39-1.17 (m, 8H), 0.86 (t, 3H)

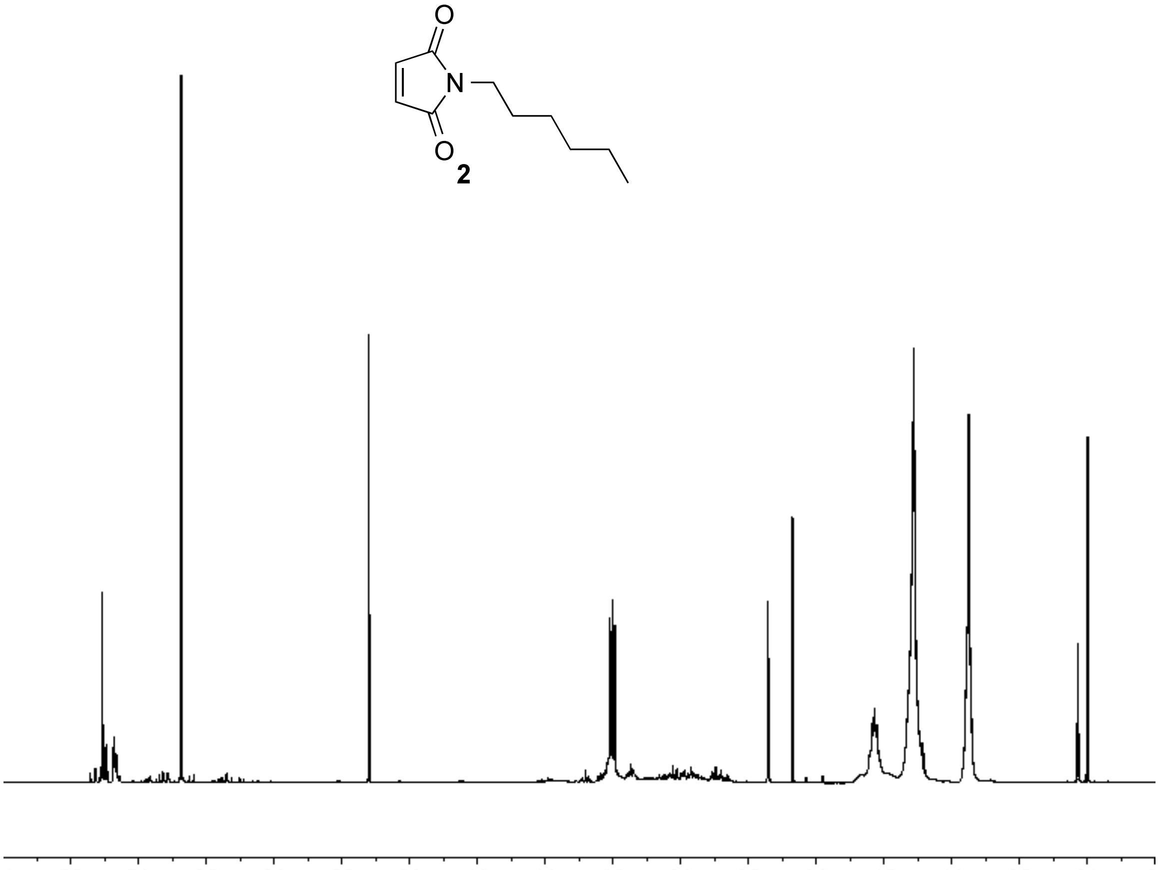


Figure S12 ^1H NMR of Compound 2

Synthesis of M6: 1.5 g of N-Hexyl Maleimide and 0.936 mL of Furan were placed in a microwave reactor with 10 mL of water. Reaction was heated to 90°

C for 1 hour. DCM was added to the mixture and organic layer was extracted and dried with $MgSO_4$. Product was used without further purification. Yield 0.195 g (9.52%). ^{1}H NMR (400 MHz $CDCl_3$): δ 6.52 (s, 2H), 5.27 (s, 2H), 2.83 (t, 2H), 1.34-1.28 (m, 8H), 0.87 (t, 3H)

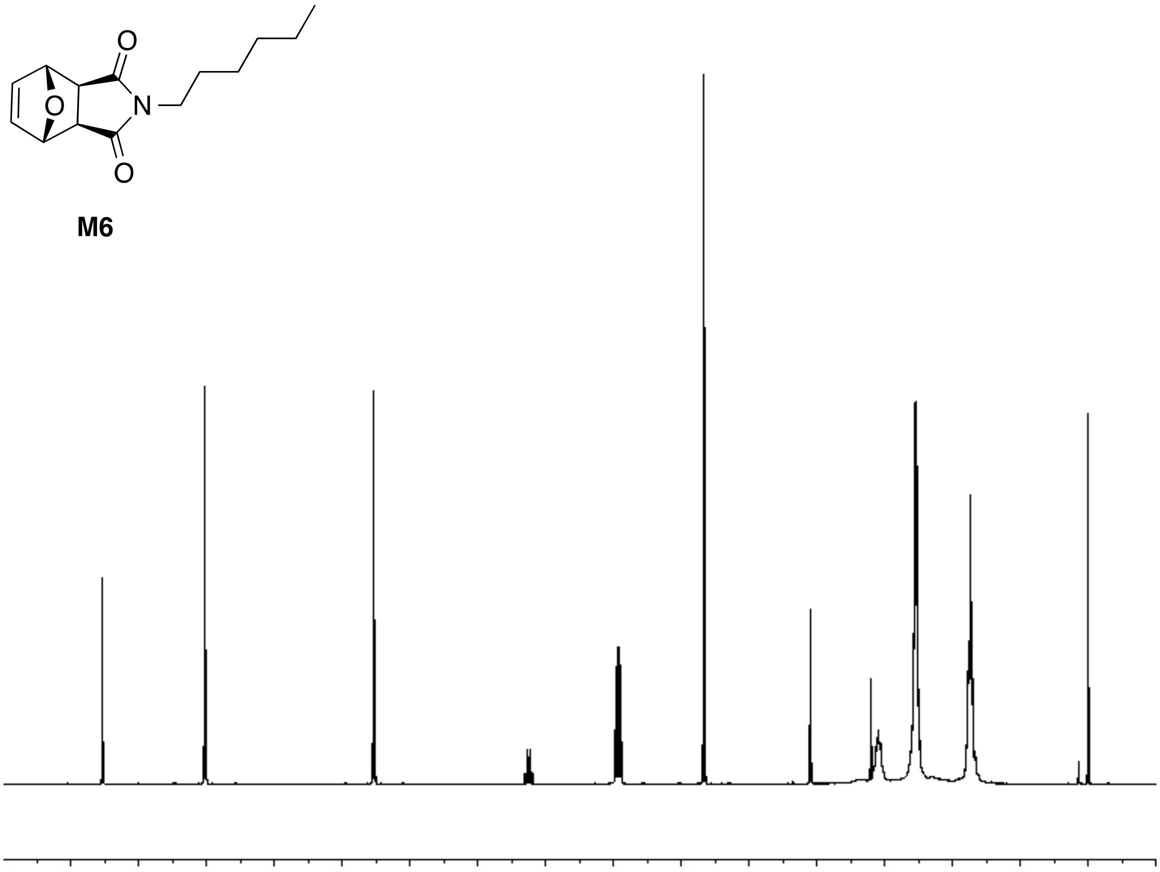


Figure S13 ^{1}H NMR of M6

General ROMP Procedure: In a 20 mL scintillation vial, Grubbs' third generation catalyst (1 eq) was dissolved in 1 mL of THF. The solution was degassed via sparging with argon for 15 minutes. Norbornene-exo-dicarboximide monomers were dissolved in dry THF and added via syringe to the solution. The reaction was run at room temp for 15 minutes and then quenched with excess ethyl vinyl ether. The polymer was then precipitated into room temperature methanol and isolated as a gummy solid with quantitative yield.

General Collapse Procedure: Polymer was dissolved in toluene to a concentration of 0.5 mg/mL. Solution was sparged with argon for 15 minutes. AIBN was dissolved in toluene and added to the solution. The reaction was heated at 80° C overnight. Toluene was then removed via rotary evaporation and nanoparticles were dissolved in DCM and precipitated into room temperature methanol. Product was recovered as gummy white solid in quantitative yield.

General Rigorous Oxygen Free Collapse Procedure: Polymer dissolved in toluene to a concentration of 0.5 mg/mL. AIBN was added to polymer solution. Solution was then degassed by multiple freeze, pump, thaw cycles (until visible gas evolution ceased) and then backfilled with argon. The reaction was heated at 80° C overnight. Solution was cooled and excess BHT was added to quench the reaction. Toluene was then removed via rotary evaporation and product dissolved in DCM and precipitated into room temperature methanol. Product was recovered as a gummy white solid in quantitative yield.

Hydrogenation Procedure: 1.00 g of Polymer and p-toluene sulfonyl hydrazide (3 eq calculated based on olefins) were added to 50 mL round bottom flask with 10 mL of xylenes. Triethylamine (3 eq) was added and solution was refluxed at 140° C for three hours. At this point solution was cooled and another portion of PTSH and TEA was added to the round bottom flask. The solution was refluxed again for three hours and then cooled and precipitated into room temperature methanol. Product was recovered as gummy white solid in quantitative yield.

Post Polymerization DCC: 0.5 g of polymer, dicyclohexyl carbodiimide (1.5 eq), and dimethyl aminopyridine (0.1 eq) were added to 100 mL round bottom flask with 20 mL of dry DCM. Methacrylic acid (1.2 eq) was added via syringe and solution was stirred overnight. The white precipitate was removed by filtration and the polymer was precipitated into room temperature methanol. Product was recovered as a white gummy solid in quantitative yield.

Polymer P1: ^{1}H NMR (400 MHz $CDCl_3$): δ 6.10-6.02 (br m), 5.84-5.65 (br m), 5.62-5.40 (br m), 4.43-4.19 (br m), 3.87-3.67 (br m), 3.52-2.54 (br m), 2.37-1.80 (br m), 1.74-1.35 (br m), 0.97-0.78 (br m). dn/dc: 0.1357 M_w: 135,000 g/mol

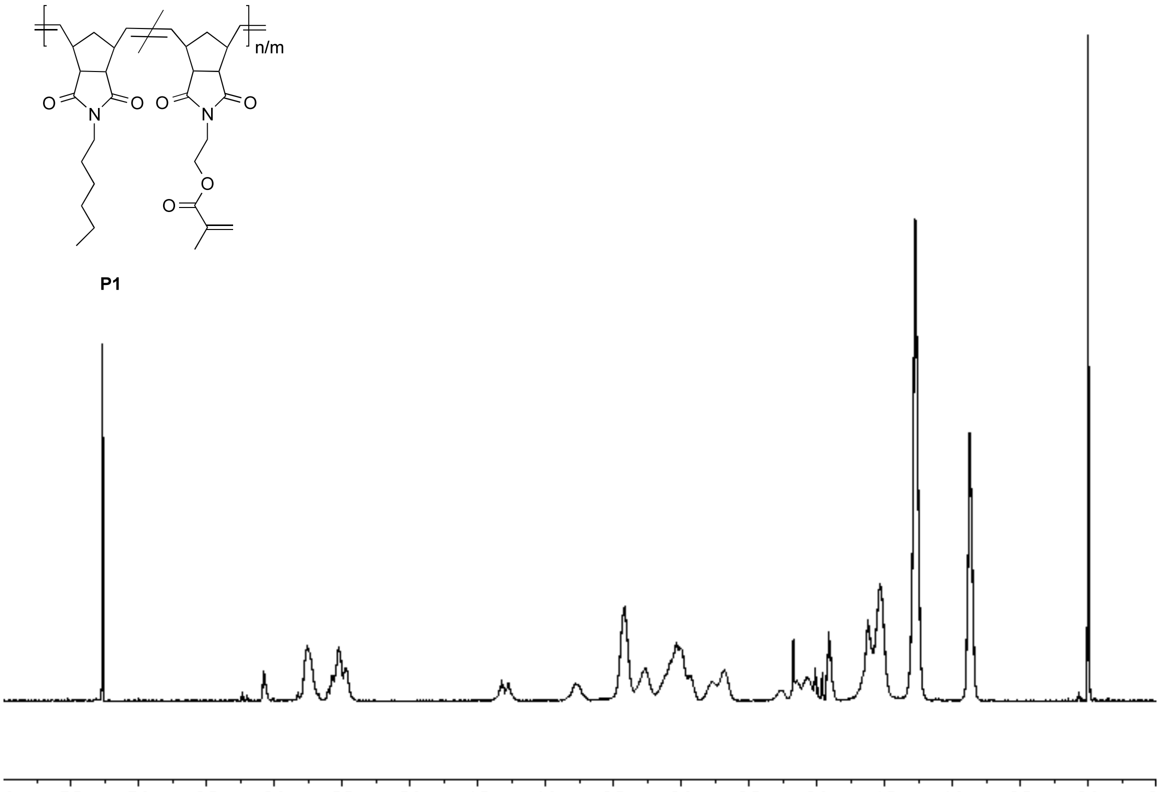


Figure S14 ^{1}H NMR of Polymer P1

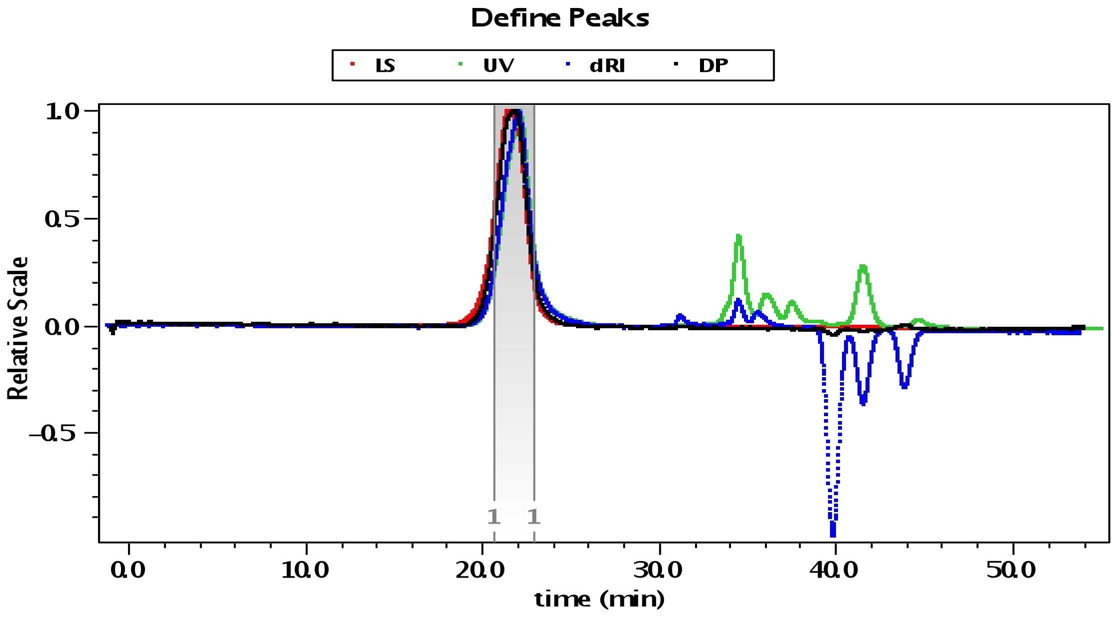


Figure S15 GPC Trace of Polymer P1

Polymer P2: ^{1}H NMR (400 MHz $CDCl_3$): δ 5.86-5.60 (br m), 5.58-5.33 (br m), 3.66-2.55 (br m), 2.32-1.94 (br m), 1.73-1.41 (br m), 1.36-1.15 (br m), 0.90-0.77 (br m). ^{13}C NMR (101 MHz $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) ? 178.51, 133.77, 132.88, 132.20, 131.98, 131.72, 77.59, 77.47, 77.27, 76.95, 53.19, 52.79, 52.62, 51.95, 51.16, 51.04, 46.46, 46.07, 43.06, 42.43, 42.17, 41.81, 41.54, 41.07, 39.12, 38.95, 38.77, 31.65, 31.59, 31.51, 27.86, 26.86, 26.77, 26.65, 22.73, 22.69, 14.24, 0.22. dn/dc: 0.1331 M_w: 121,000 g/mol

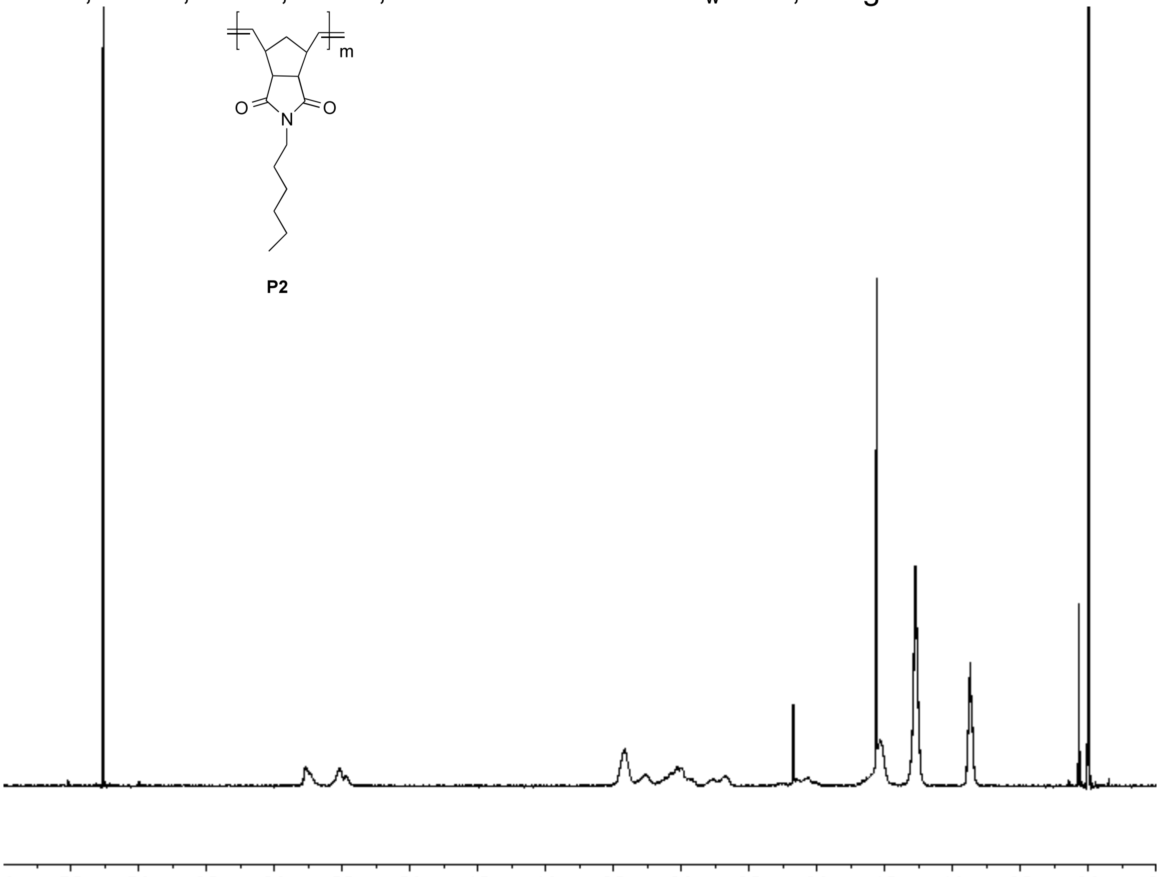


Figure S16 ^{1}H NMR of Polymer P2

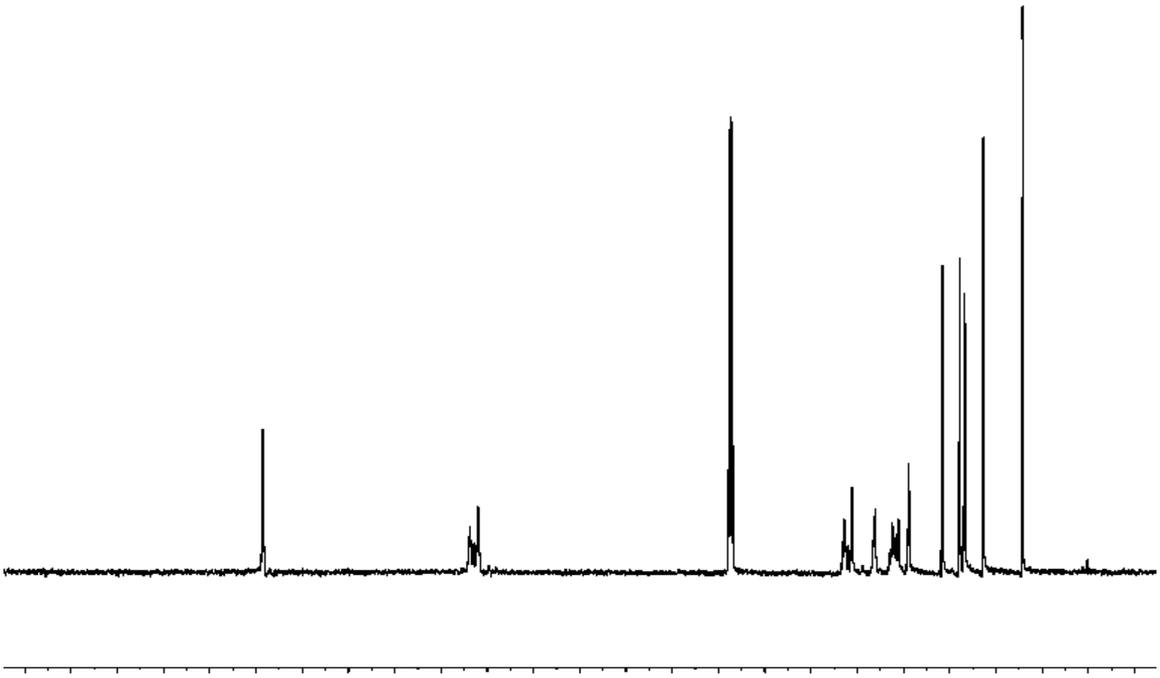


Figure S17 ^{13}C NMR of Polymer P2

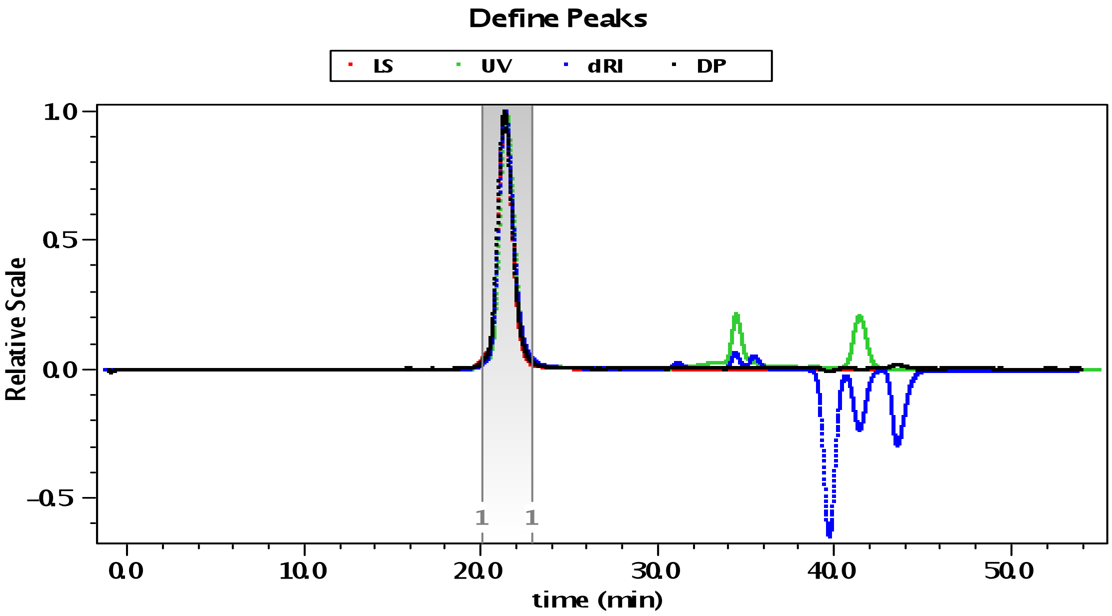


Figure S18 GPC Trace of Polymer P2

Polymer P2H: ^{1}H NMR (400 MHz $CDCl_3$): δ 3.52-3.35 (br m), 2.88-2.71 (br m), 2.40-2.15 (br m), 2.06-1.76 (br m), 1.71-1.41 (br m), 1.41-0.61 (br m). dn/dc: 0.1213 M_w: 140,000 g/mol

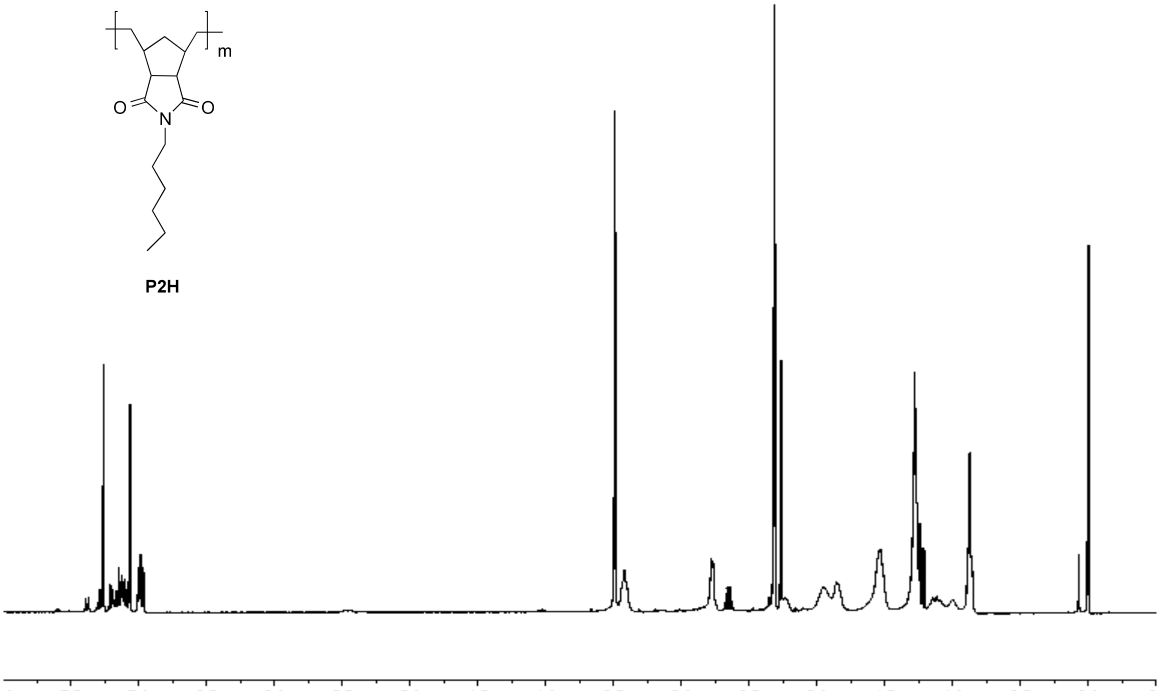


Figure S19 ^{1}H NMR of Polymer P2H

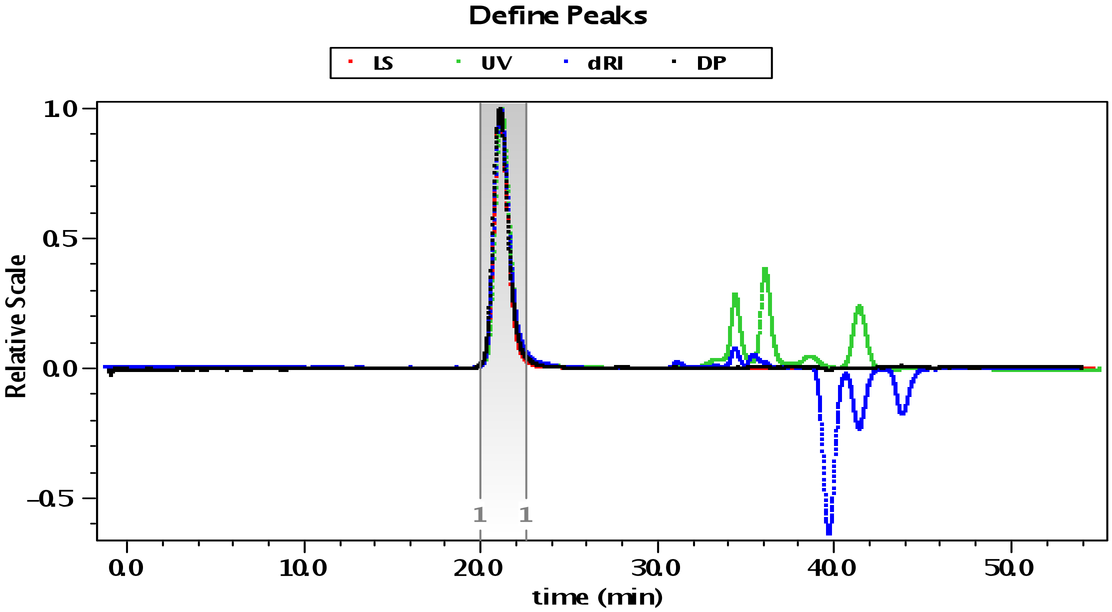
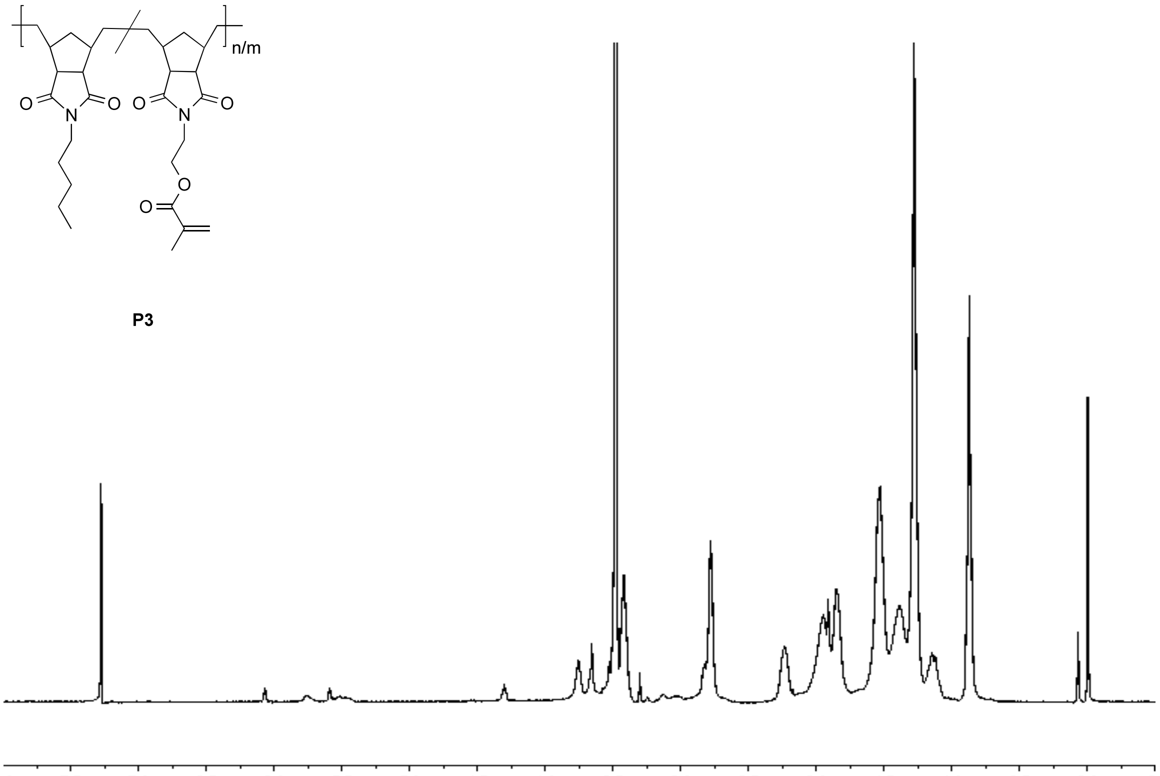


Figure S20 GPC Trace of Polymer P2H

Polymer P3: ^{1}H NMR (400 MHz $CDCl_3$): δ 6.10-6.05 (br m), 5.78-5.68 (br m), 5.61-5.38 (br m), 4.34-4.26 (br m), 3.86-2.62 (br m), 2.35-1.03 (br m), 0.93-0.78 (br m). dn/dc: 0.1612 M_w: 59,000 g/mol



P3

Figure S21 ^{1}H NMR of Polymer P3

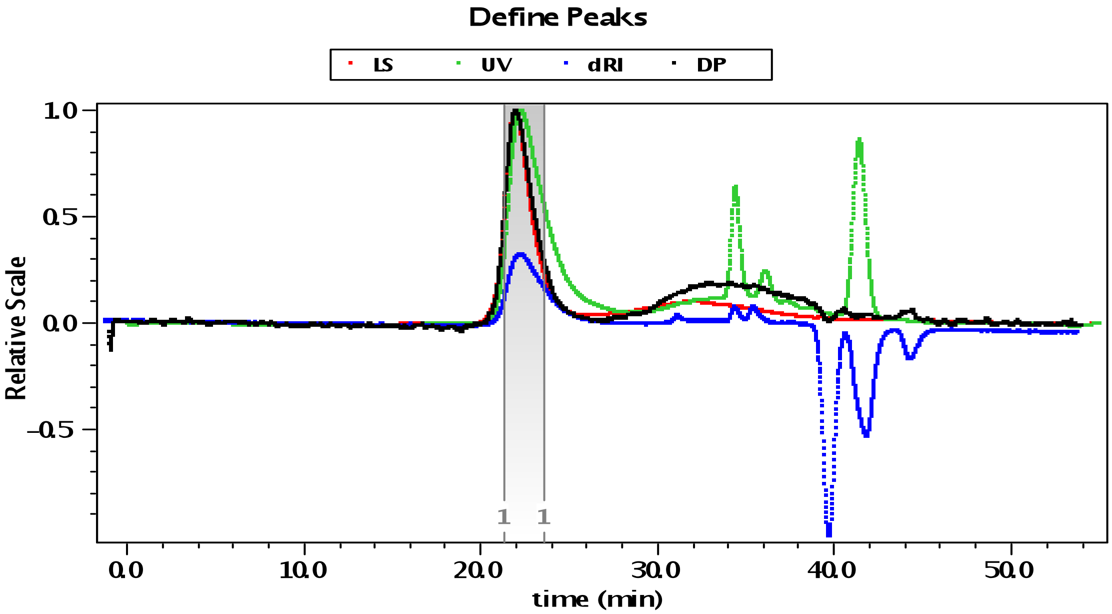


Figure S22 GPC Trace of Polymer P3

Poly Oxa NBI: ^{1}H NMR (400 MHz $CDCl_3$): δ 6.10-6.02 (br m), 5.87-5.67 (br m), 5.14-4.94 (br m), 4.59-4.39 (br m), 3.55-3.22 (br m), 1.65-1.48 (br m), 1.40-1.06 (br m), 0.93-0.72 (br m). dn/dc: 0.1158 M_w: 177,000

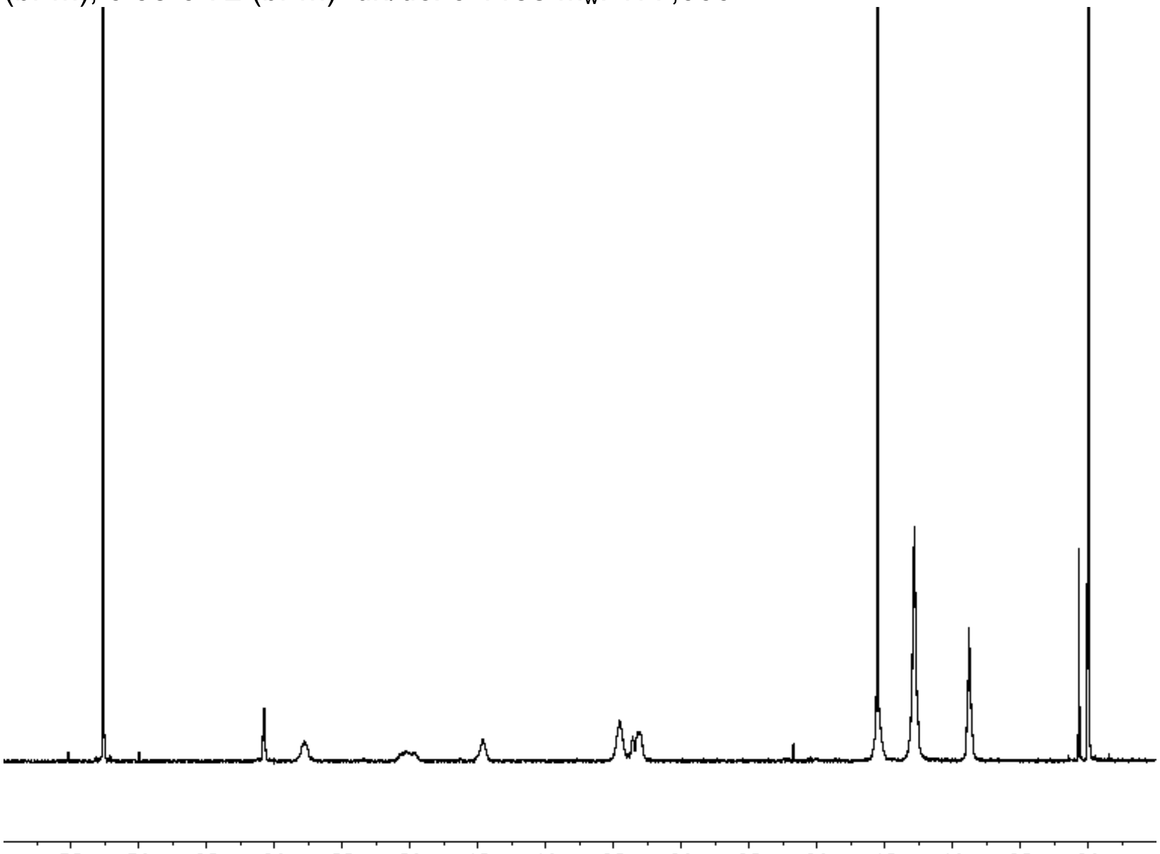


Figure S23 ^{1}H NMR of Poly Oxa NBI

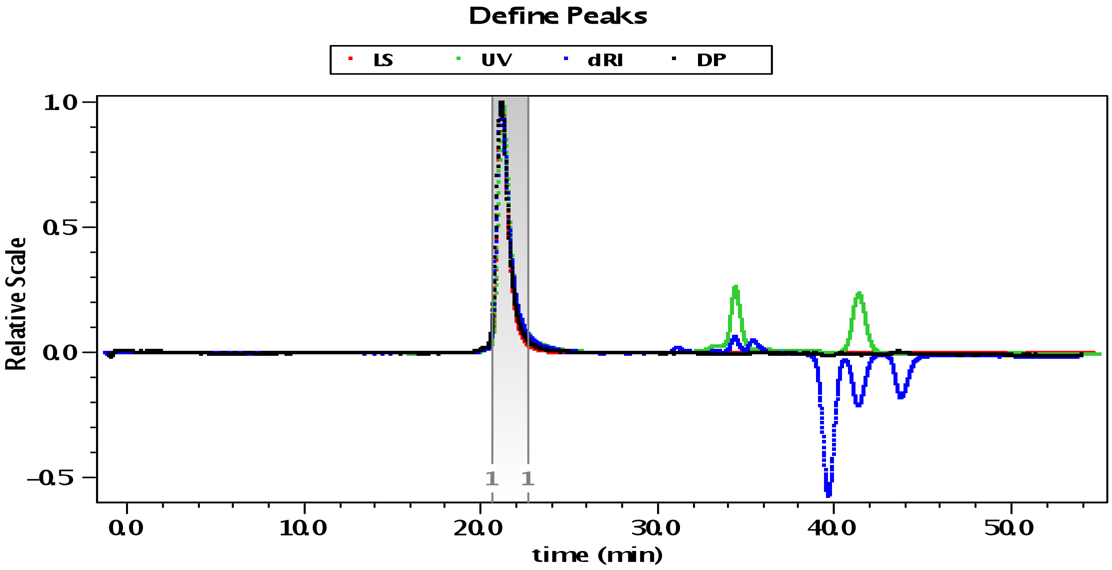


Figure S24 GPC Trace of Poly Oxa NBI

Poly NBI-OH: ^{1}H NMR (400 MHz $CDCl_3$): δ 5.83-5.66 (br m), 5.63-5.42 (br m), 3.86-2.61 (br m), 2.36-1.76 (br m), 1.73-1.39 (br m), 1.35-1.09 (br m), 0.95-0.77 (br m). dn/dc: 0.1660 M_w: 62,000 g/ mol

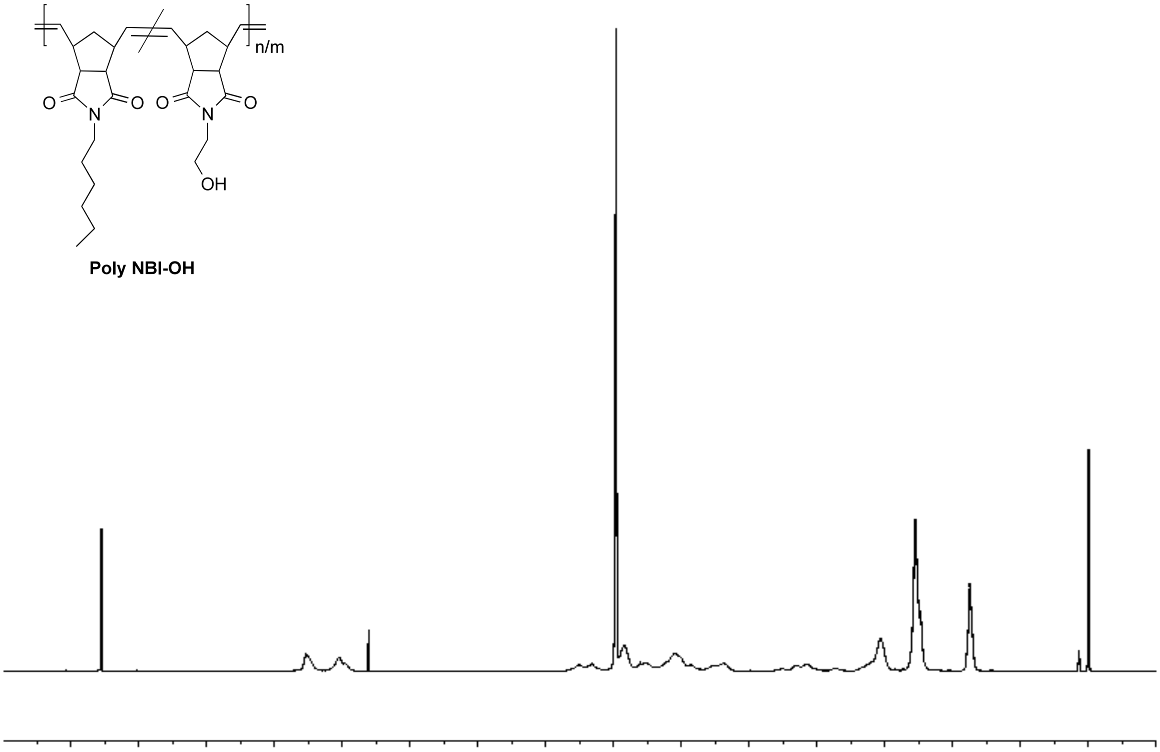


Figure S25 ^{1}H NMR of Poly NBI-OH

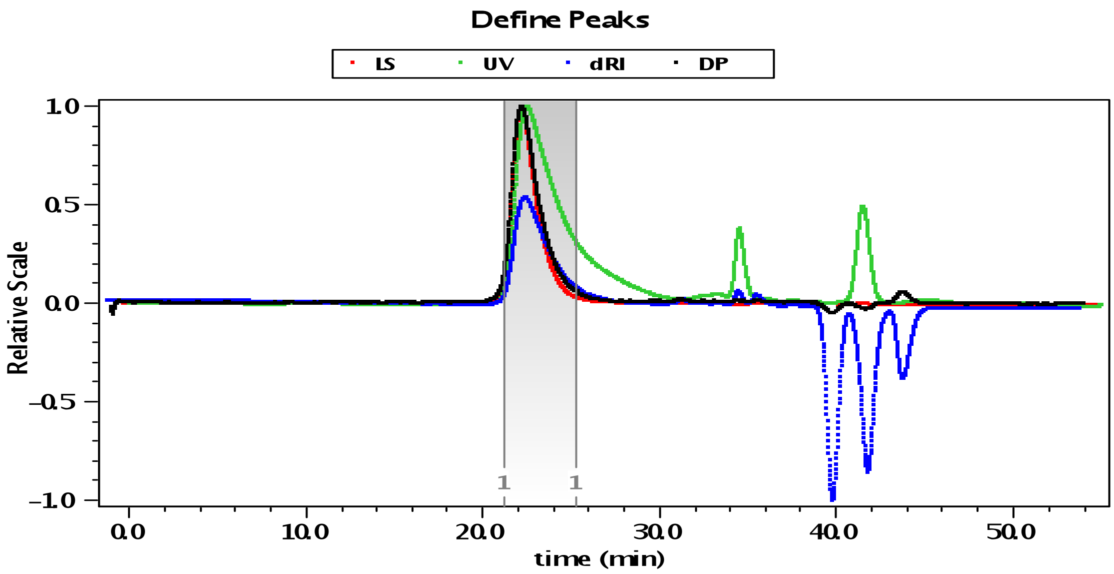


Figure S26 GPC Trace of Poly NBI-OH

Hydrogenated Poly NBI-OH: ^{1}H NMR (400 MHz CDCl$_3$): δ 3.80-3.31 (br m), 2.92-2.71 (br m), 2.38-2.16 (br m), 2.07-1.76 (br m), 1.65-1.04 (br m), 0.93-0.80 (br m). dn/dc: 0.1612 M$_w$: 61,000 g/mol

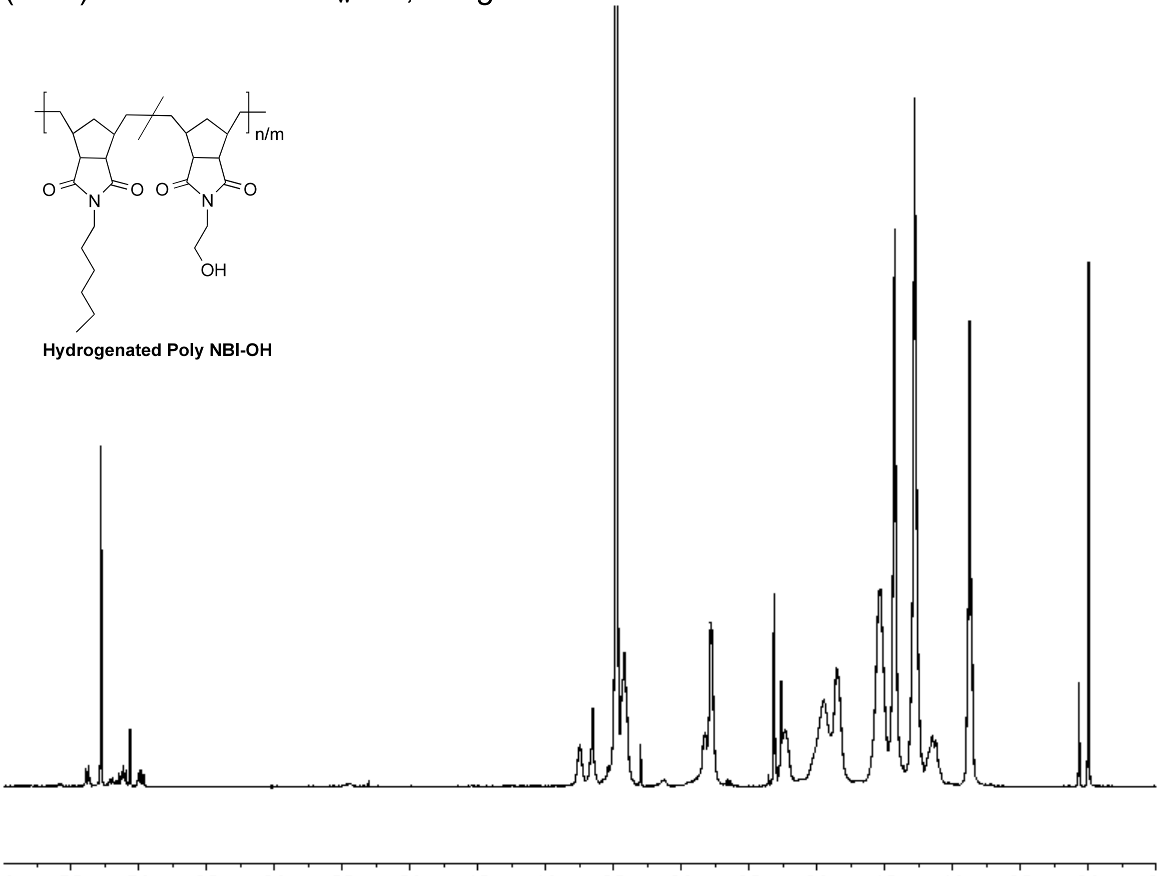


Figure S27 ^{1}H NMR of Hydrogenated Poly NBI-OH

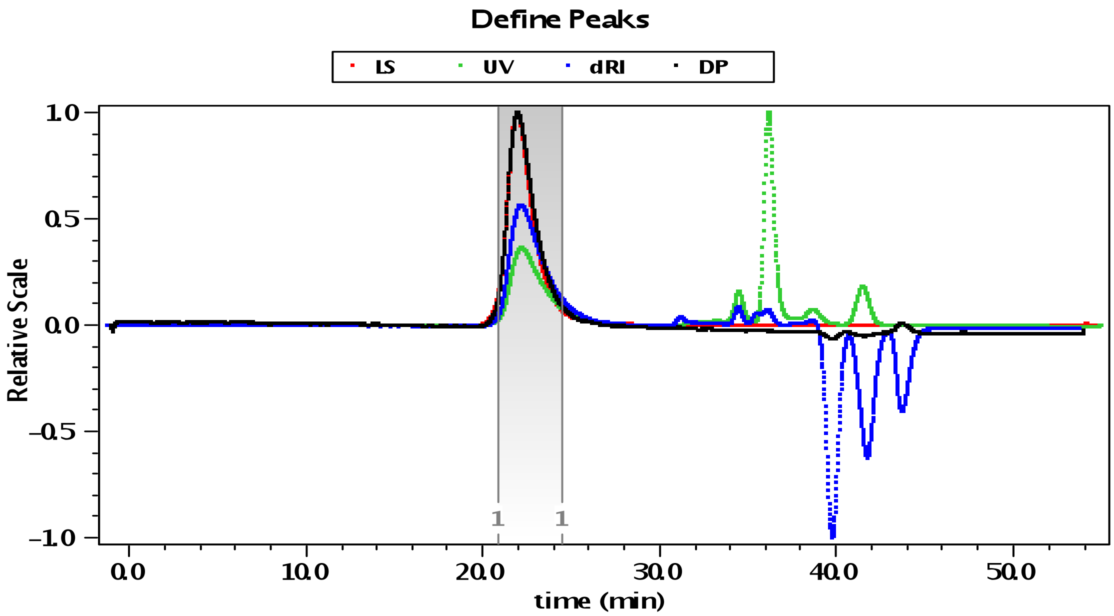


Figure S28 GPC Trace of Hydrogenated Poly NBI-OH

Nanoparticle NP1: ^{1}H NMR (400 MHz $CDCl_3$): δ 6.10-6.02 (br m), 5.84-5.65 (br m), 5.62-5.40 (br m), 4.43-4.19 (br m), 3.87-3.67 (br m), 3.52-2.54 (br m), 2.37-1.80 (br m), 1.74-1.35 (br m), 0.97-0.78 (br m). dn/dc: 0.1357

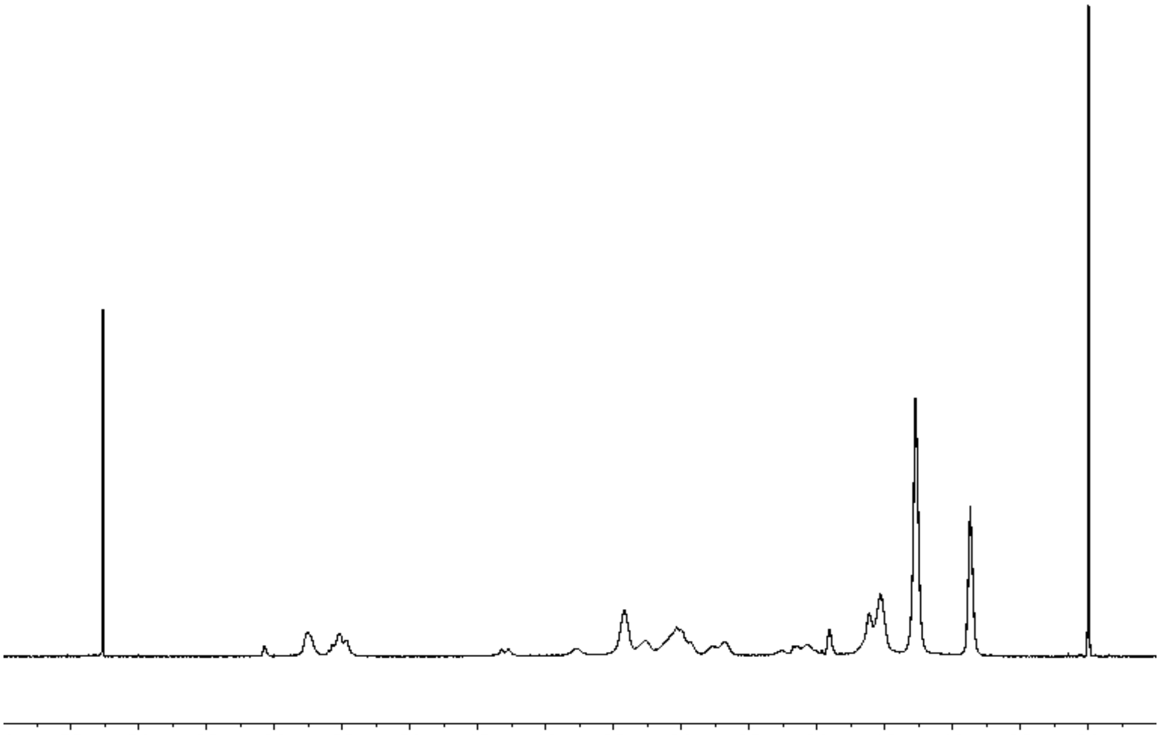


Figure S29 ^{1}H NMR of Nanoparticle NP1

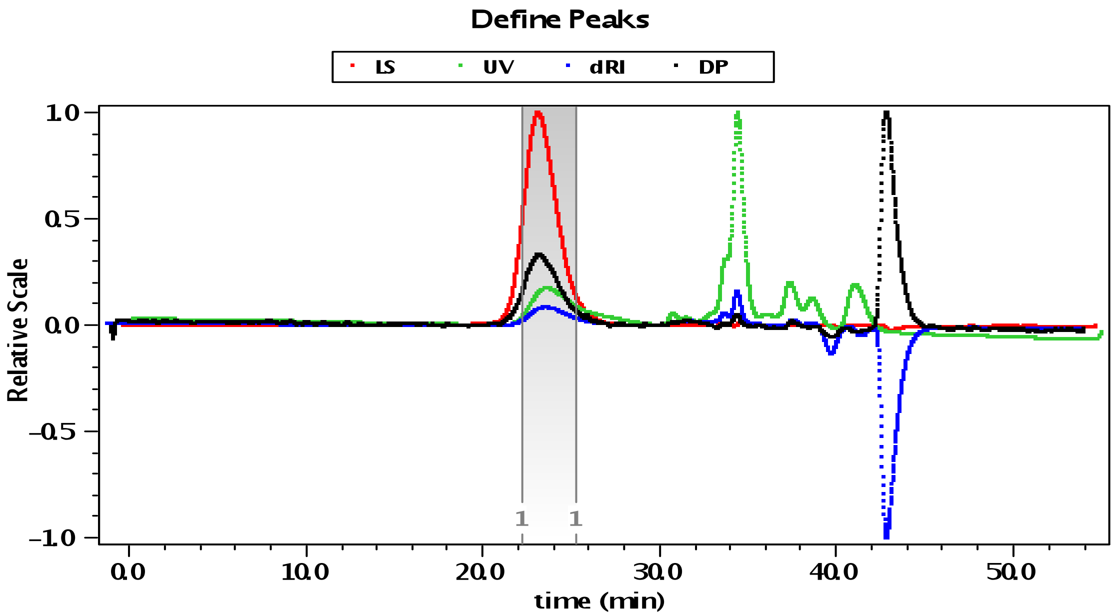


Figure S30 GPC Trace of Nanoparticle NP1

Nanoparticle NP2: ^{1}H NMR (400 MHz CDCl$_3$): δ 5.86-5.60 (br m), 5.58-5.33 (br m), 3.66-2.55 (br m), 2.32-1.94 (br m), 1.73-1.41 (br m), 1.36-1.15 (br m), 0.90-0.77 (br m). ^{13}C NMR (101 MHz CDCl$_3$): ^{13}C NMR (101 MHz, CDCl$_3$) ? 178.51, 133.77, 132.88, 132.20, 131.98, 131.72, 77.59, 77.47, 77.27, 76.95, 53.19, 52.79, 52.62, 51.95, 51.16, 51.04, 46.46, 46.07, 43.06, 42.43, 42.17, 41.81, 41.54, 41.07, 39.12, 38.95, 38.77, 31.65, 31.59, 31.51, 27.86, 26.86, 26.77, 26.65, 22.73, 22.69, 14.24, 0.22. dn/dc: 0.1331

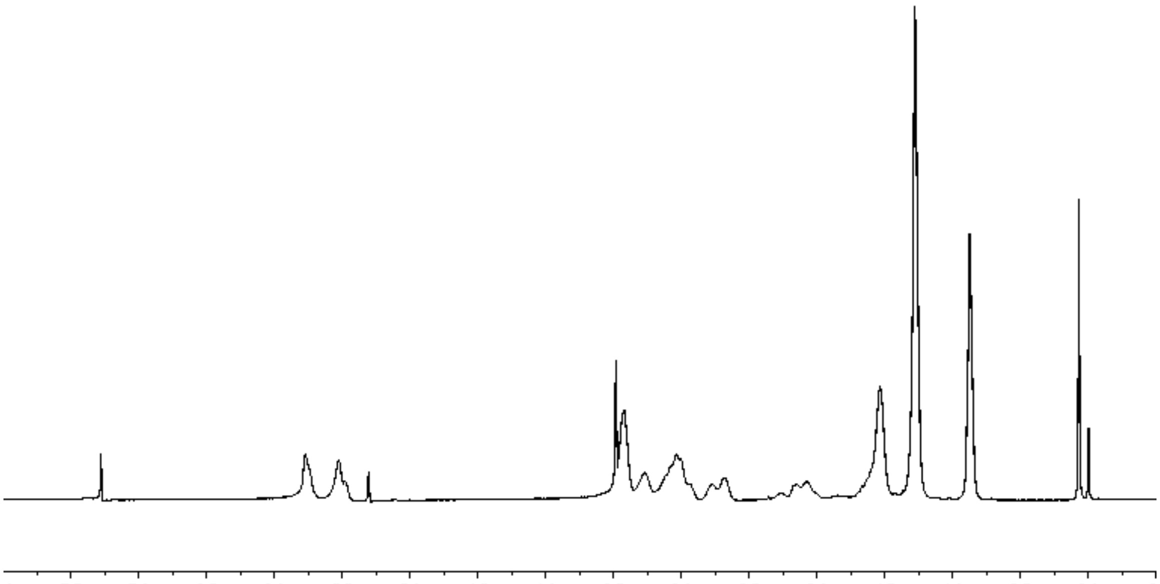


Figure S31 ^{1}H NMR of Nanoparticle NP2

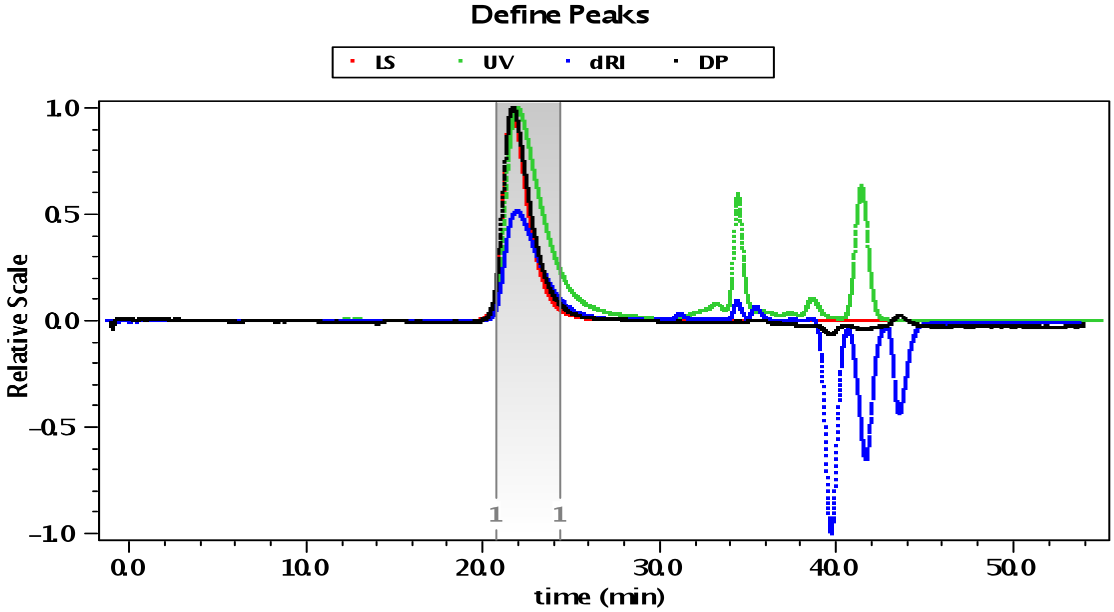


Figure S32 GPC Trace of Nanoparticle NP2

Nanoparticle NP3: ^{1}H NMR (400 MHz CDCl$_3$): δ 6.10-6.05 (br m), 5.78-5.68 (br m), 5.61-5.38 (br m), 4.34-4.26 (br m), 3.86-2.62 (br m), 2.35-1.03 (br m), 0.93-0.78 (br m). dn/dc: 0.1612

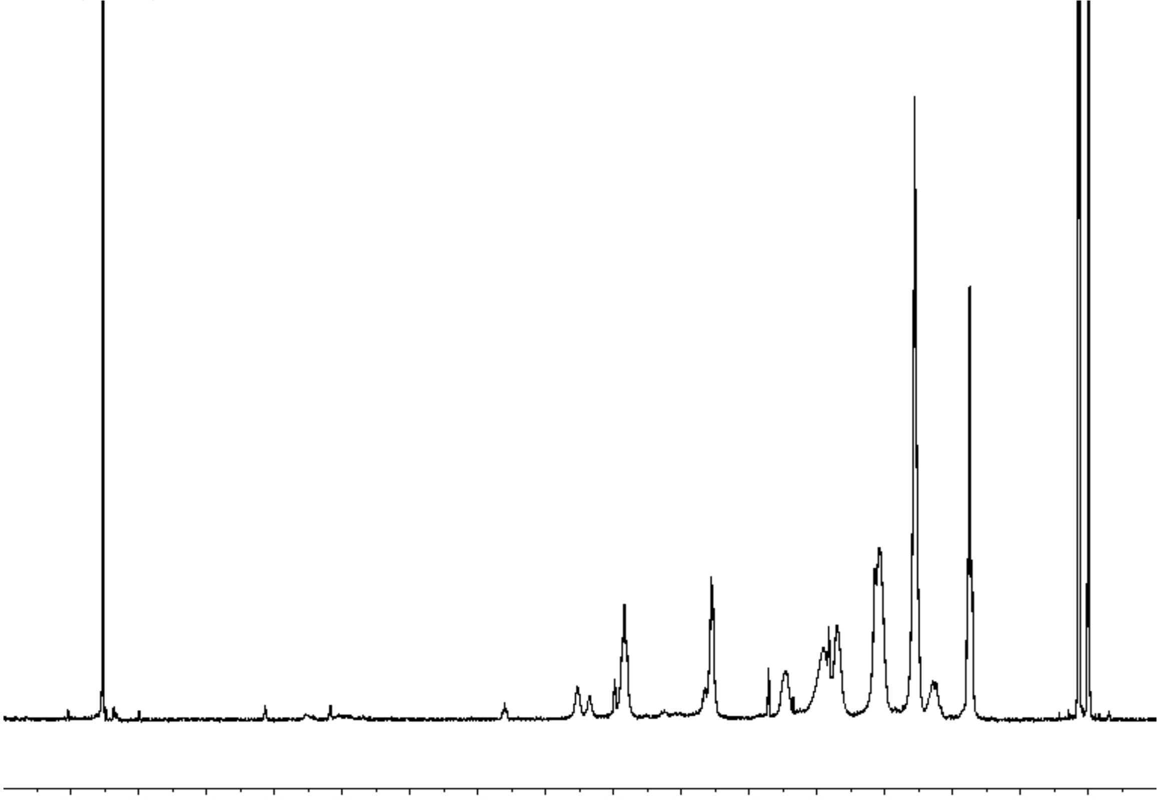


Figure S33 ^{1}H NMR of Nanoparticle NP3

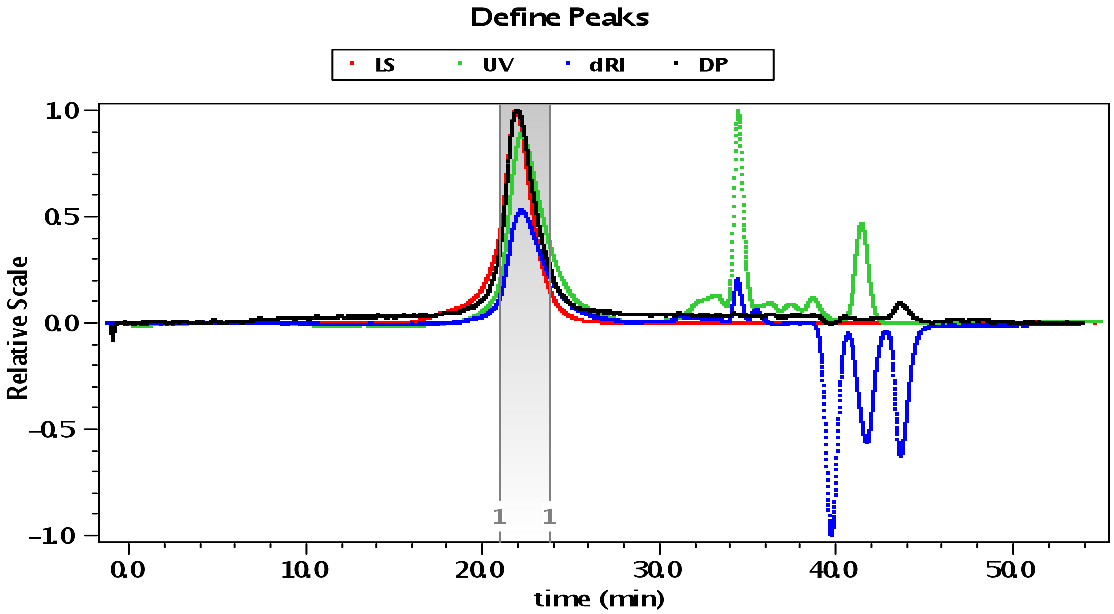


Figure S34 GPC Trace of Nanoparticle NP3

Nanoparticle NP1-FPT: ^{1}H NMR (400 MHz CDCl$_3$): δ 6.10-6.02 (br m), 5.84-5.65 (br m), 5.62-5.40 (br m), 4.43-4.19 (br m), 3.87-3.67 (br m), 3.52-2.54 (br m), 2.37-1.80 (br m), 1.74-1.35 (br m), 0.97-0.78 (br m). dn/dc: 0.1357

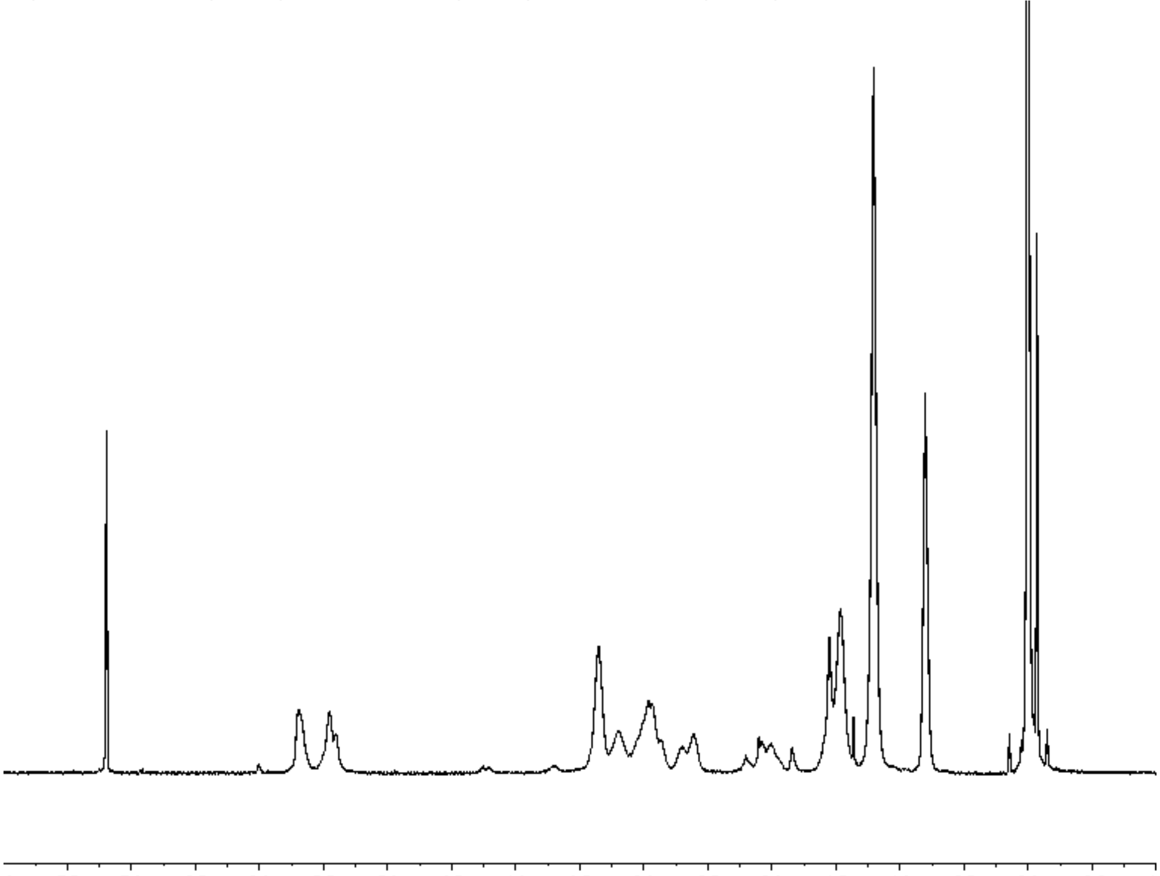


Figure S35 ^{1}H NMR of NP1-FPT

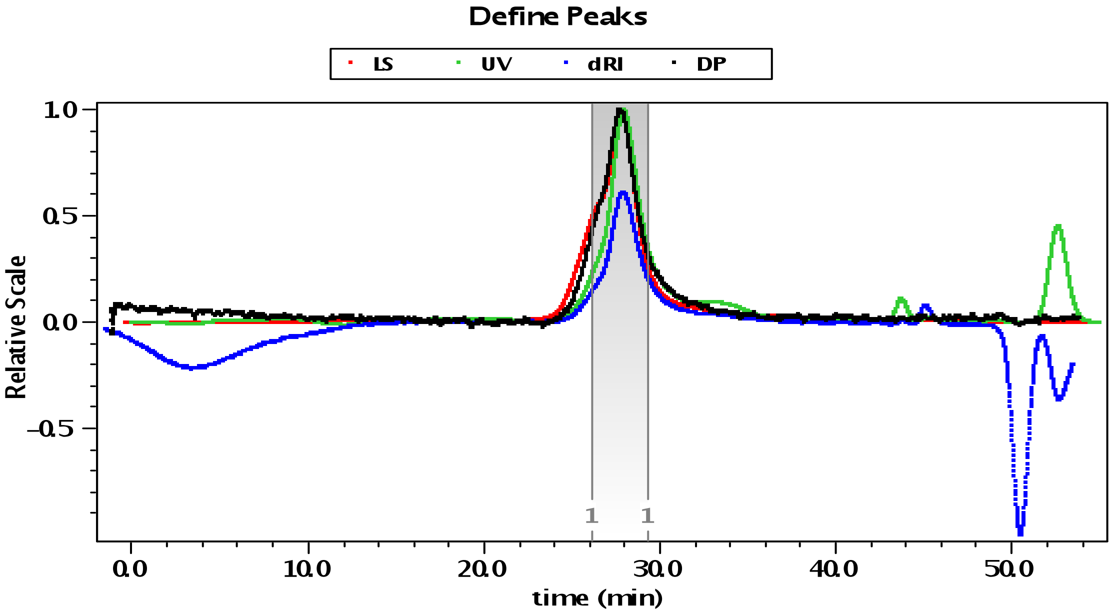


Figure S36 GPC Trace of Nanoparticle NP1-FPT

Nanoparticle NP2-FPT

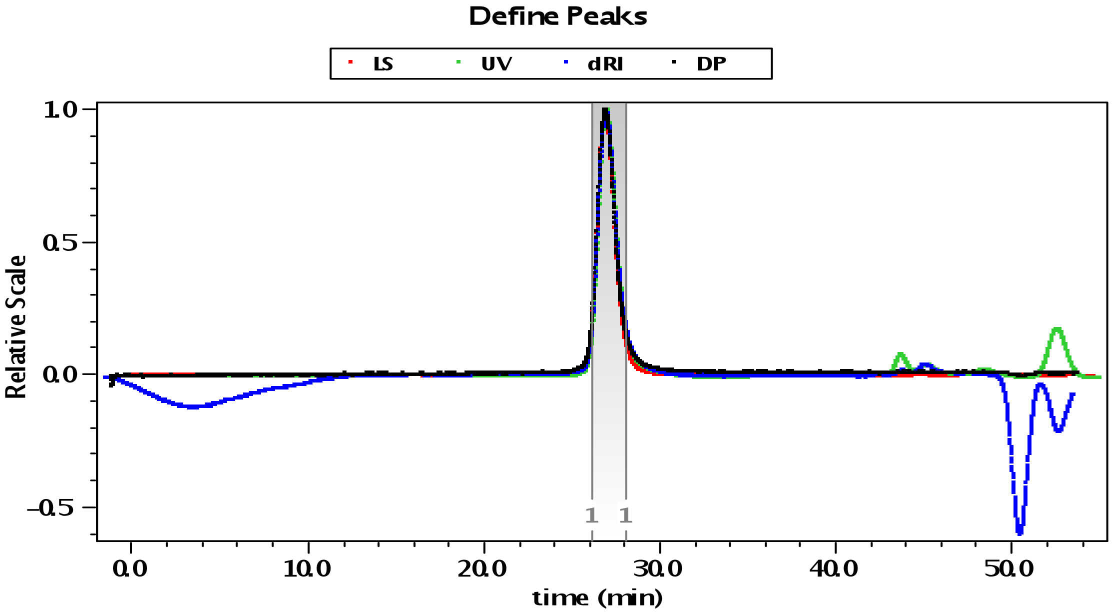


Figure S37 GPC Trace of Nanoparticle NP2-FPT

Nanoparticle NP3-FPT

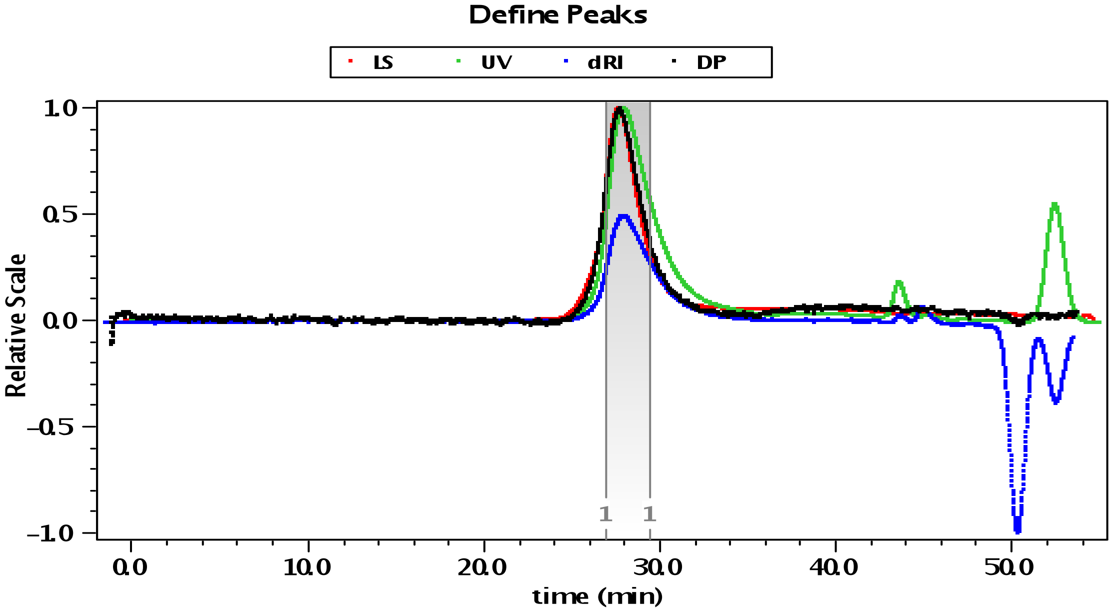


Figure S38 GPC Trace of Nnoparticle NP3-FPT

Sample	dn/dc	Mw (g/mol)	Mw/Mn
P1	0.1357	135,000	1.09
P2	0.1331	121,000	1.01
P2h	0.1213	140000	1.02
P3	0.0545	175000	1.12
P2 200k	0.1024	204000	1.01
P1 (for FPT)	0.1437	116000	1.02

Table S1: SEC data on parent polymers

Note on SEC data: All parent polymer molecular weights correspond well with predicted values. We've found that reliable nanoparticle dn/dc values are very difficult to obtain for these polymers, based largely on the dilute conditions and vanishing amounts of material we are working with. This makes accurate absolute molecular weight data difficult to obtain for this particular system. In this report we rely on the size exclusion effect of our instrument to confirm changes in hydrodynamic volume. Based on triplicate runs of PS standards of several molecular weights we've determined the error in retention time of our instrument to be +/- .05 min. All of the shifts reported here fall well outside of this range.

References:

1) Reference: J. Am. Chem. Soc., **2008**, 130, 6731-6733