

One-Pot Synthesis of Linear Triblock Terpolymers and their Aqueous Self-Assembly

Eman Ahmed,^a C. Tyler Womble,^a Jinwon Cho,^b Kristen Dancel-Manning,^c Dr. William J. Rice,^d Seung Soon Jang*^b and Marcus Weck*^a

^{a.} *Molecular Design Institute, Department of Chemistry, New York University, New York, NY, 10003, USA. E-mail: marcus.weck@nyu.edu*

^{b.} *School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Dr., Atlanta, GA 30332-0245, USA. E-mail: seungsoon.jang@mse.gatech.edu*

^{c.} *OCS Microscopy Core, New York University Langone Medical Center, New York, NY, 10016, USA.*

^{d.} *Cryo-Electron Microscopy Laboratory, New York University Langone Medical Center, New York, NY, 10016, USA.*

Table of Contents

Materials and Methods.....	3
Syntheses.....	5
Grubbs' Third Generation Initiator Synthesis.....	5
Monomer Syntheses.....	5
ROMP Polymerization Procedure.....	10
General ROMP Procedure.....	10
Representative Ring-Opening Metathesis Polymerization.....	11
ROMP Kinetics Experiments.....	11
NMR Spectra.....	15
Gel Permeation Chromatography.....	22
Homopolymers.....	22
Subsequent block incorporation.....	22
Triblock terpolymers.....	24
Differential Scanning Calorimetry.....	25
Percent Composition Calculation.....	26
Dynamic Light Scattering Analysis.....	27
Table S 1. Summary of particle sizes obtained by DLS.....	27
Particle Size Distributions by DLS.....	28
Cryogenic Transmission Electron Microscopy.....	30

References31

Materials and Methods. All reactions and manipulations of compounds were carried out in air unless otherwise specified. CDCl_3 , CD_2Cl_2 , Acetone- d_6 , DMSO- d_6 , CD_3OD , and CD_3OH were purchased from Cambridge Isotope Laboratories (CIL) and used as received. All reagents and solvents were purchased from commercial sources and used as received unless otherwise specified.

NMR Analysis. All NMR spectra were recorded on either a 400 or 500 MHz Bruker Advance Spectrometer. The ^1H NMR spectra were referenced to residual protio solvents (7.26 ppm for CHCl_3 , 5.32 ppm for CHDCl_2 , 4.79 for DOH, 3.31 ppm for CHD_2OD , 3.31 ppm for CHD_2OH , 2.50 ppm for DMSO- d_5 , and 2.05 ppm for Acetone- d_5) and $^{13}\text{C}\{^1\text{H}\}$ NMR were referenced to the solvent signal (CDCl_3 : 77.23 ppm, CD_2Cl_2 : 54.00 ppm, DMSO- d_6 : 39.51 ppm, and Acetone- d_6 : 29.92 ppm). The $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were electronically referenced using internal Bruker software according to a universal scale determined from the precise ratio, Ξ , of the resonance frequency of the ^{19}F nuclide to the ^1H resonance of TMS in a dilute solution ($\varphi < 1\%$).

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry of the prepared samples was performed on a PerkinElmer DSC 8000 instrument. Thermograms were run in a nitrogen atmosphere, applying heating–cooling–heating runs between -80 and 200 °C with a rate of 60 °C min^{-1} . The thermograms of the second heating ramp were analyzed. Temperature and heat flow were calibrated using standard materials (indium and zinc) at cooling and heating rates of 10 °C min^{-1} .

Dynamic Light Scattering (DLS). Particle size measurements were performed on a Malvern Zetasizer Nano using a scattering angle $\theta = 173^\circ$ (backscattering detection) and a He-Ne laser with a wavelength of 633 nm.

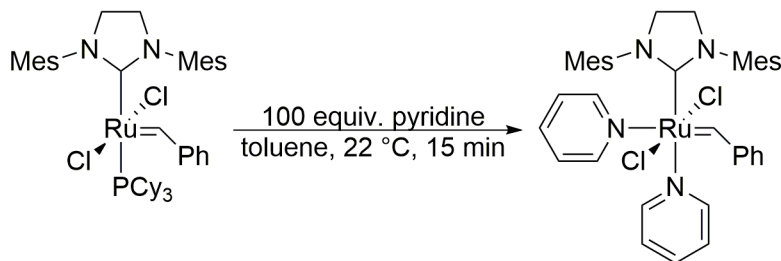
Cryogenic Transmission Electron Microscopy. 400 Mesh holey carbon grids were purchased from Ted Pella and plasma treated for 60 s using Nanoclean (Fischione) before use. Cryo-TEM grids were prepared in an FEI Vitrobot at 19 °C with the relative humidity set to 100 % and the blotting force set to 4.3 μL of the polymer micelle solution was pipetted onto a freshly glow-discharged grid. The sample solution was incubated on the grid for 10 s, blotted for 2 s before being plunged into liquid ethane that was pre-cooled by liquid nitrogen. The Cryo-TEM grids were then transferred in liquid nitrogen into a Gatan 626 cryo-specimen holder and then inserted into the microscope. The specimen temperature was maintained at -170 °C during data collection. Cryo-TEM imaging was performed in an FEI TITAN Halo TEM operating at 300 kV and recorded in the low dose mode ($20 \text{ e}^-/\text{\AA}^2$) on an FEI CETA 10M camera ($4,096 \times 4,096$ pixel).

Cryogenic Electron Tomography. Arctica operated at 200 kV with a GatanK3 imaging system collected at 22,000X nominal magnification. The calibrated super-resolution pixel size of 0.9330 \AA was used for processing. Tilt series movies were collected using SerialEM at a dose rate of 4.90 $\text{e}^-/\text{\AA}^2/\text{s}$. Each movie was 8 frames at 70 ms/frame, for a total dose per tilt of 2.74 $\text{e}^-/\text{\AA}^2$. Number of tilt series: 19; tilt range: -51° to $+51^\circ$; tilt increment: 3° ; constant exposure for each image; collection strategy: Bidirectional from 0° , unidirectional past 40° tilt.

Gel-Permeation Chromatography (GPC). was carried out using a Shimadzu pump coupled to a Shimadzu RI detector, controlled by an EZStart program. A set of American Polymer Standards columns (AM GPC gel, 10 μm , precolumn, 500 \AA and linear mixed bed) was used with a 0.03 M LiCl solution in N,N-dimethylformamide at a flow rate of 1 mL/ min at 60 °C or with tetrahydrofuran at a flow rate of 1mL/min at 22 °C. The system was calibrated with poly(styrene) standards (EasiCal, Agilent Technologies, Santa Clara, CA).

Syntheses

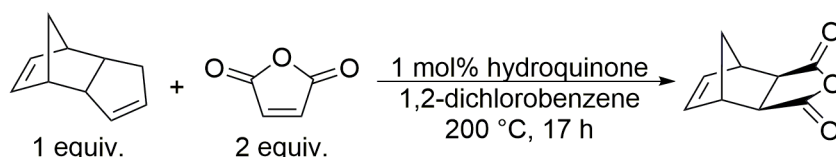
Grubbs' Third Generation Initiator



$[(\text{H}_2\text{IMes})(\text{pyr})_2(\text{Cl})_2\text{Ru}=\text{CHPh}]$ was prepared according to a published report.¹

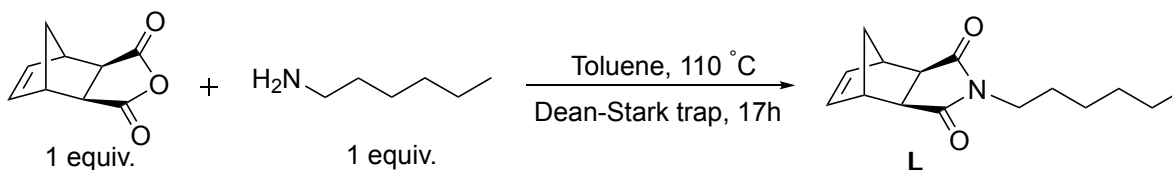
$[(\text{H}_2\text{IMes})(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CHPh}]$ (250 mg, 0.3 mmol) was dissolved in 0.5 mL of anhydrous toluene. Pyridine (2.45 mL, 30.4 mmol) was added and the reaction mixture color rapidly changed from red-brown to dark green. The mixture was stirred for 15 minutes before adding 20 mL of pentane. The solution was cooled to 0 °C in a refrigerator and let stand for 17 h. The precipitate was carefully filtered and the solids were washed with cold pentane (3 × 5 mL). The bright green product was dried for 8 hours under vacuum and stored under an inert atmosphere (174 mg, 80 % yield).

Monomer Syntheses

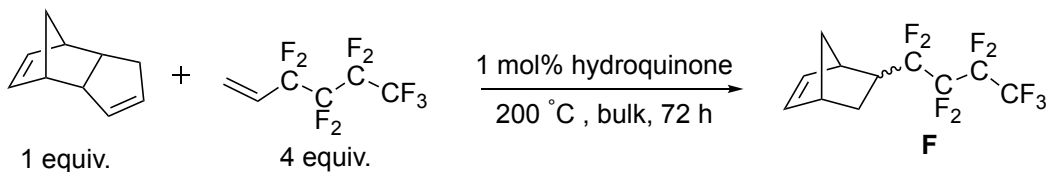


cis-5-norbornene-*exo*-2,3-dicarboxylic anhydride, was prepared according to modified literature reports.^{2,3} Dicyclopentadiene (8.19 g, 62.0 mmol), maleic anhydride (11.59 g, 118 mmol), hydroquinone (65.0 mg, 0.6 mmol), and 1,2-dichlorobenzene (50 mL) were added to a 250 mL pressure tube. The contents of the tube were sealed and heated to 200 °C using an oil bath for 17 hours. The reaction mixture was cooled and the solvent was removed under vacuum. The solid residue was filtered and washed with cold methanol. The crude product was recrystallized from ethyl acetate (3×) to give a white, crystalline solid that was dried under vacuum for 6 h (2.42 g, 22

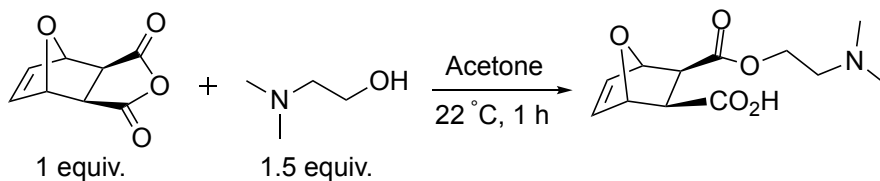
% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.32 (s, 2H), 3.44 (t, $J = 1.8$ Hz, 2H), 2.99 (d, $J = 1.5$ Hz, 2H), 1.75 – 1.59 (m, 1H), 1.50 – 1.34 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 171.8, 138.1, 48.9, 47.0, 44.3.



***N*-hexyl-*exo*-norbornene-5,6-dicarboximide, L**, was prepared according to a modified literature report.⁴ *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (2.62 g, 16.0 mmol) was added to 100 mL of anhydrous toluene in a 250 mL round bottomed flask equipped with a reflux condenser and Dean Stark trap. *N*-hexylamine (2.1 mL, 16.0 mmol) was added to the flask and the reaction mixture was heated to reflux for 17 hours using an oil bath. The flask was cooled to 22 °C and the solvent was removed under vacuum. The residue was diluted with 50 mL of dichloromethane and was washed with 50 mL of 10% (v/v) HCl, 50 mL of water, and 50 mL of brine solution. The organic layer was dried over anhydrous sodium sulfate and then concentrated by rotary evaporation. The crude product was purified via flash column chromatography with hexane/ethyl acetate (1:2) using silica gel to yield a clear oil (3.24 g, 82 % yield). The product was further dried for 8 h under high vacuum. ^1H NMR (400 MHz, CDCl_3) δ 6.27 (t, $J = 1.7$ Hz, 2H), 3.44 (t, $J = 7.5$ Hz, 2H), 3.26 (t, $J = 1.6$ Hz, 2H), 2.65 (d, $J = 1.1$ Hz, 2H), 1.58 – 1.46 (m, 3H), 1.33 – 1.20 (m, 7H), 0.89 – 0.83 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 178.3, 138.0, 48.0, 45.3, 42.9, 38.9, 31.5, 27.9, 26.8, 22.6, 14.2.

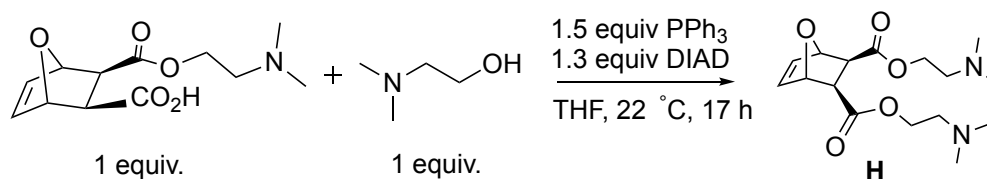


endo/exo-5-(perfluorobutyl)bicyclo[2.2.1]hept-2-ene, F, was prepared according to modified literature reports.^{5,6} Dicyclopentadiene (0.67 g, 5.1 mmol), 1H,1H,2H-perfluoro-1-hexene (5.0 g, 20.3 mmol), and hydroquinone (6.0 mg, 0.05 mmol) were added to a 10 mL Schlenk bomb flask. The flask was sealed and the reaction mixture was heated to 200 °C using an oil bath for 72 hours. The flask was then cooled to 22 °C and residual 1H,1H,2H-perfluoro-1-hexene was removed under vacuum. The residue was vacuum distilled (100 mtorr, 40 °C) to isolate the product as a clear oil, which was redistilled for further purification (1.41 g, 89 % yield, *endo:exo* = 3:1). ¹H NMR (mixture of *endo/exo*, 400 MHz, CDCl₃) δ 6.27 – 5.89 (2H), 3.16 (m, 1H), 3.05 – 2.89 (m, 1H), 2.88 – 2.68 (m, 1H), 2.17 – 1.91 (m, 1H), 1.57 – 1.43 (m, 1H), 1.43 – 1.17 (m, 2H). ¹³C{¹H} NMR (mixture of *endo/exo*, 101 MHz, CDCl₃) δ 138.5, 137.5, 136.6, 132.0, 49.9, 46.6, 43.9, 42.6, 42.2, 41.5, 41.4 – 40.9 (m), 40.4 (t, *J* = 19.5 Hz), 27.8, 27.0. ¹⁹F{¹H} NMR (mixture of *endo/exo*, 377 MHz, CDCl₃) δ -80.3 – -81.9 (m, 3F), -110.6 – -117.1 (m, 2F), -121.8 – -123.5 (m, 2F), -124.7 – -127.9 (m, 2F).



(1S,2R,3S,4R)-3-((2-(Dimethylamino)ethoxy)carbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid was prepared according to a published report.⁷ *cis*-5-Oxanorbornene-*exo*-2,3-dicarboxylic anhydride (10.0 g, 60.2 mmol) and acetone (100 mL) were added to a 250 mL round bottomed flask. *N,N*-dimethylethanolamine (9.0 mL, 90.3 mmol) was added dropwise over a period of 30 minutes. The reaction mixture was stirred for one hour at 22 °C. The precipitate was

filtered and washed with cold acetone (2 × 50 mL) and the solid was dried *in vacuo* at 50 °C for four hours. The product was obtained as a colorless solid and was used without further purification (13.8 g, 90% yield). ¹H NMR (400 MHz, D₂O) δ 6.77 – 6.35 (m, 2H), 5.44 – 5.06 (m, 2H), 4.49 (m, 2H), 3.46 (m, 2H), 2.95 – 2.93 (m, 7H), 2.85 (d, *J* = 9.3 Hz, 1H). ¹³C{¹H} NMR (101 MHz, D₂O) δ 215.3, 179.9, 174.3, 137.2, 135.5, 81.1, 79.6, 58.4, 56.1, 49.9, 46.5, 42.9, 30.2.



***exo,exo*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-di**

(*N,N*-dimethyl)aminoethanolato

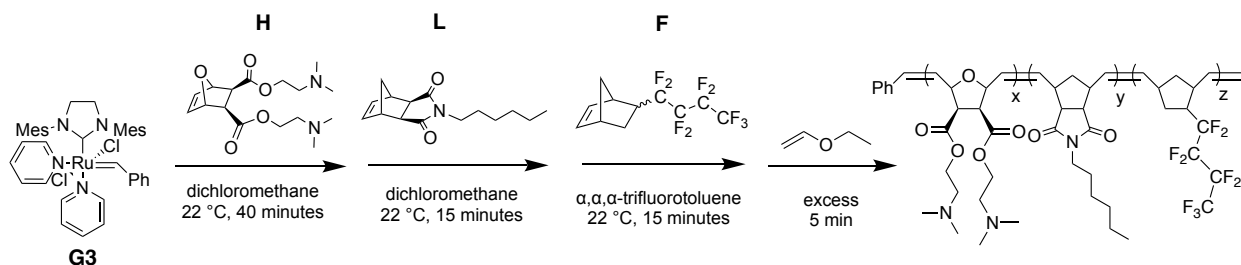
dicarboxylate, H, was prepared according to a published report. (1*S*,2*R*,3*S*,4*R*)-3-((2-(dimethylamino)ethoxy)carbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (4.1 g, 16.1 mmol), triphenylphosphine (5.0 g, 19.0 mmol), *N,N*-dimethylethanolamine (1.9 mL, 19.0 mmol), and anhydrous THF (40 mL) were added to a 150 mL Schlenk flask and put under N₂. The contents of the flask were cooled to 0 °C using an ice bath and then diisopropylazodicarboxylate (DIAD) (3.7 mL, 18.8 mmol) dissolved in 10 mL anhydrous THF was added dropwise over one hour. The reaction mixture was gradually warmed to 22 °C and stirred for 17 hours. The mixture was then filtered and the solvent was completely removed *in vacuo*. The residue was dissolved in 25 mL of saturated citric acid solution and 50 mL ethyl acetate was added. After separation, the organic layer was removed and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The aqueous layer was neutralized to pH = 10 using potassium carbonate and was then extracted with diethyl ether (5 × 50 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated by rotary evaporation to yield the product as a clear oil (2.0 g, 38 % yield). ¹H NMR (400 MHz, CDCl₃) δ 6.44 (t, *J* = 1.0 Hz, 2H), 5.25 (t, *J* = 1.0 Hz, 2H), 4.33 – 4.06 (m, 4H),

2.84 (s, 2H), 2.61 – 2.50 (m, 4H), 2.27 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 171.7, 136.8, 80.8, 62.9, 57.8, 47.0, 45.9.

ROMP Polymerization Procedure

General ROMP Procedure

Scheme S1. Triblock terpolymers.



Ring-Opening Metathesis Polymerization to form triply amphiphilic terpolymers was conducted in a dry glovebox under a N_2 atmosphere. A 10 mg/mL stock solution of **G3** was prepared by dissolving 7.2 mg of **G3** in 0.72 mL of dry dichloromethane. A 0.1 mL aliquot of the initiator solution was added to a 20 mL scintillation vial. Stock solutions for the lipophilic monomer (**L**) and hydrophilic monomer (**H**) were prepared by dissolving the determined amount of monomer in dry dichloromethane so that the final concentration was 0.2 M. Stock solution of the fluorophilic monomer (**F**) was prepared by dissolving the determined amount of monomer in dry, distilled α, α, α -trifluorotoluene so that the final concentration was 0.1 M. The overall total monomer concentration was 0.2 M. Polymerization was initiated by injecting the calculated amount of monomer solution into the catalyst solution under vigorous stirring at 22 °C. The color of the catalyst solution quickly turned from green to brown. After 15 minutes (40 minutes for addition of **H**), a second addition of monomer was injected into the reaction mixture. This was repeated for the third monomer addition. After a final 15 minutes (or 40 minutes), approximately 100 equiv. of ethyl vinyl ether was added to quench the polymerization and the reaction mixture was stirred for five minutes. The solvent was removed by rotary evaporation and the crude polymer was purified by dialysis against acetone (1 kDa molecular weight cutoff). The contents of the dialysis bag were

transferred to a pre-weighed 20 mL scintillation vial and the solvent was removed by rotary evaporation. The remaining solid was further dried under *in vacuo* on a Schlenk line (50 mtorr) at 50 °C for two hours. The polymer was then dissolved in 1.0 mL of Acetone-*d*₆ and analyzed by NMR spectroscopy and Size Exclusion Chromatography.

Representative Ring-Opening Metathesis Polymerization

0.1 mL (10 mg/mL, 1.4 μmol) of the **G3** initiator stock solution was added to a 20 mL scintillation vial. In three separate vials, 52 mg (0.21 mmol) of **L** was dissolved in 1.00 mL of dry dichloromethane, 91 mg (0.28 mmol) of **H** was dissolved in 1.4 mL of dry dichloromethane, and 21 mg (0.07 mmol) of **F** was dissolved in 0.35 mL of α,α,α -trifluorotoluene. The monomer solution containing **F** was injected into the catalyst solution at 22 °C and was vigorously stirred for 15 minutes. Then, the monomer solution containing **H** was injected and the polymerization was stirred for 40 minutes. After a final injection of the monomer solution containing **L**, the polymerization was stirred for an additional 15 minutes and then 0.1 mL (1.0 mmol) of ethyl vinyl ether was added and the reaction mixture was stirred for five minutes. After purification, 66 mg of the triblock copolymer (77% yield) was obtained as a brown solid.

ROMP Kinetics Experiments

The rate of monomer conversion vs time was determined by ¹H NMR spectroscopy using a 30° tip angle, a 1.00 second delay, and 8 scans per time point.

A stock solution of **G3** was prepared by dissolving the initiator (4.5 mg) in 0.45 mL of deuterated dichloromethane. In a glovebox under an atmosphere of N₂, the hydrophilic monomer, **H**, (62 mg, 0.19 mmol) was added to a NMR tube along with 0.85 mL of deuterated dichloromethane. An initial spectrum was taken in order to properly lock, shim, and tune the sample. Then, the NMR cap was removed and 0.15 mL of the **G3** stock solution (1.5 mg, 2 μmol) was rapidly injected into

the sample. The cap was quickly returned, the tube was shaken several times, and the ^1H NMR spectrum was taken after a time interval of 60 seconds. Spectra were automatically taken every 60 seconds for a total time of 15 minutes. Conversion was determined from the integration of the vinyl proton signals (6.48 – 6.30 ppm) compared to the integration of the $-\text{OCH}_2-$ signals (4.22 – 3.90 ppm). A linear fit of the natural logarithm of conversion ($\ln([\text{M}]_0/[\text{M}])$) vs time was used to determine the apparent propagation rate constant (k_{app}).

Kinetics experiments for the lipophilic monomer **L** was performed in a similar manner. **L** (42 mg, 17 mmol) was added to an NMR tube and was dissolved in 0.85 mL of deuterated dichloromethane. A 0.15 mL aliquot of the **G3** stock solution (1.5 mg, 2 μmol) was rapidly injected into the sample and ^1H NMR spectra were collected every 60 seconds. Conversion was determined from the integration of the vinyl proton signals (6.29 – 6.16 ppm) compared to the integration of the $-\text{CH}_3$ proton signal (0.93 – 0.70 ppm).

Kinetics experiments for the fluorophilic monomer **F** were similar as described above except that deuterated toluene was used to dissolve the monomer due to the insolubility of the homopolymer in dichloromethane. **F** (60 mg, 19 mmol) was added to an NMR tube and 0.85 mL of deuterated toluene was added. A 0.15 mL aliquot of the **G3** stock solution (1.5 mg, 2 μmol) was rapidly injected into the sample and ^1H NMR spectra were collected every 60 seconds. Conversion was determined from the integration of the vinyl proton signals (5.91 – 5.66 ppm) compared to the integration of the aromatic protons from the residual protio solvent (7.14 – 6.86 ppm).

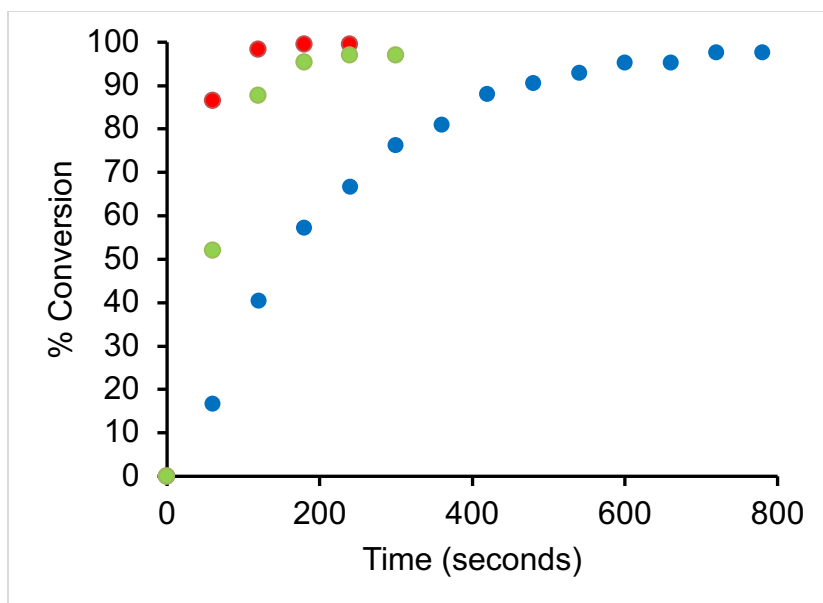


Figure S 1. Plot of conversion vs time for the hydrophilic (blue), lipophilic (red), and fluorophilic (green) monomers.

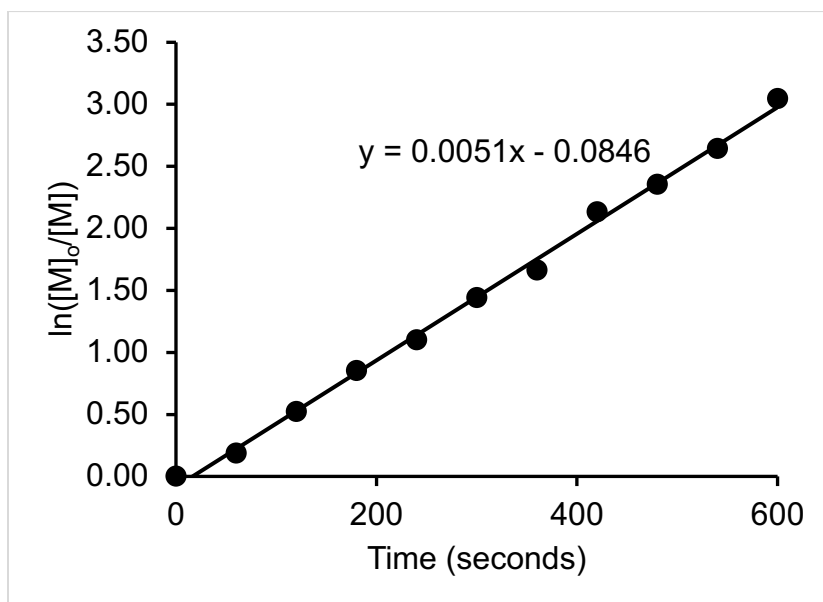


Figure S 2. Plot of $\ln([M]_0/[M])$ vs time for the ROMP of **H**.

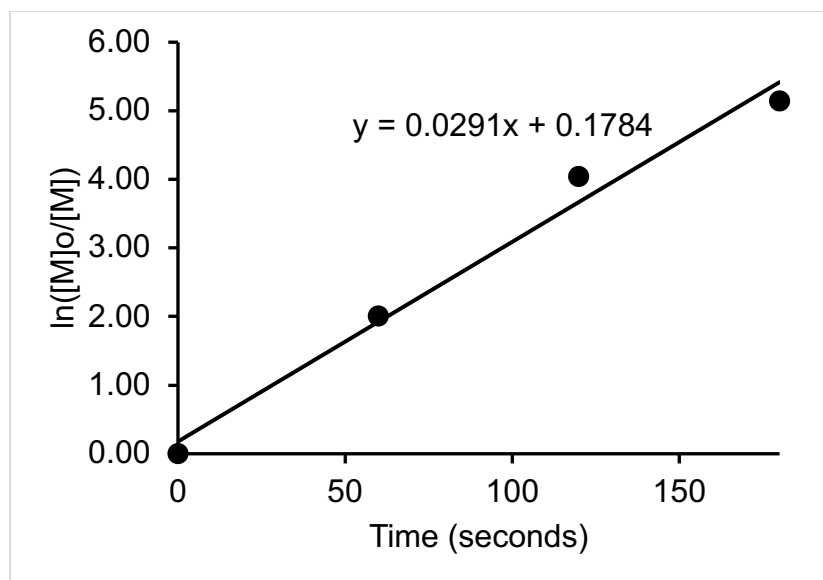


Figure S 3. Plot of $\ln([M]_0/[M])$ vs time for the ROMP of **L**.

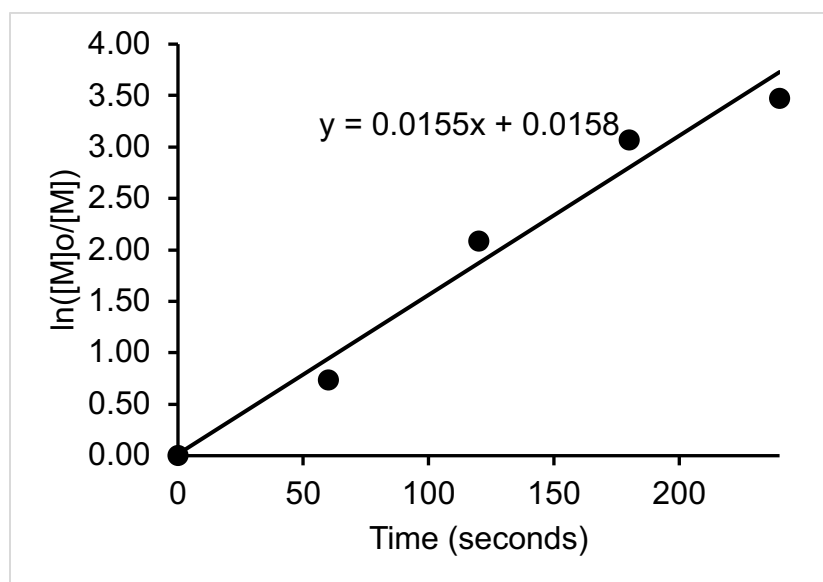


Figure S 4. Plot of $\ln([M]_0/[M])$ vs time for the ROMP of **F**.

NMR Spectra

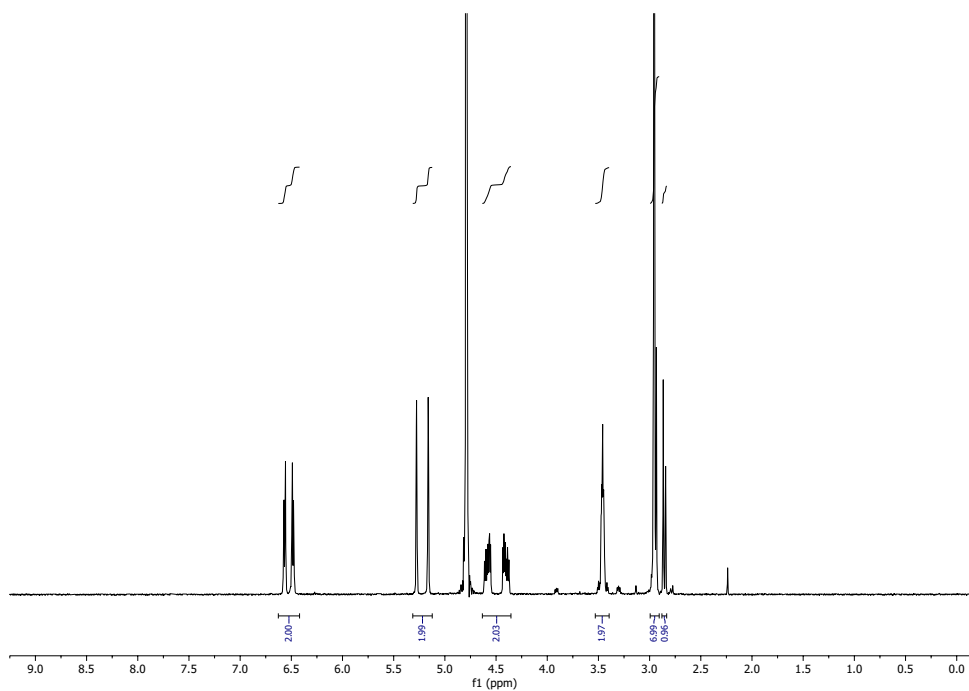


Figure S 5. ¹H NMR spectrum of (1S,2R,3S,4R)-3-((2-(dimethylamino)ethoxy)carbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid. D₂O, 400 MHz.

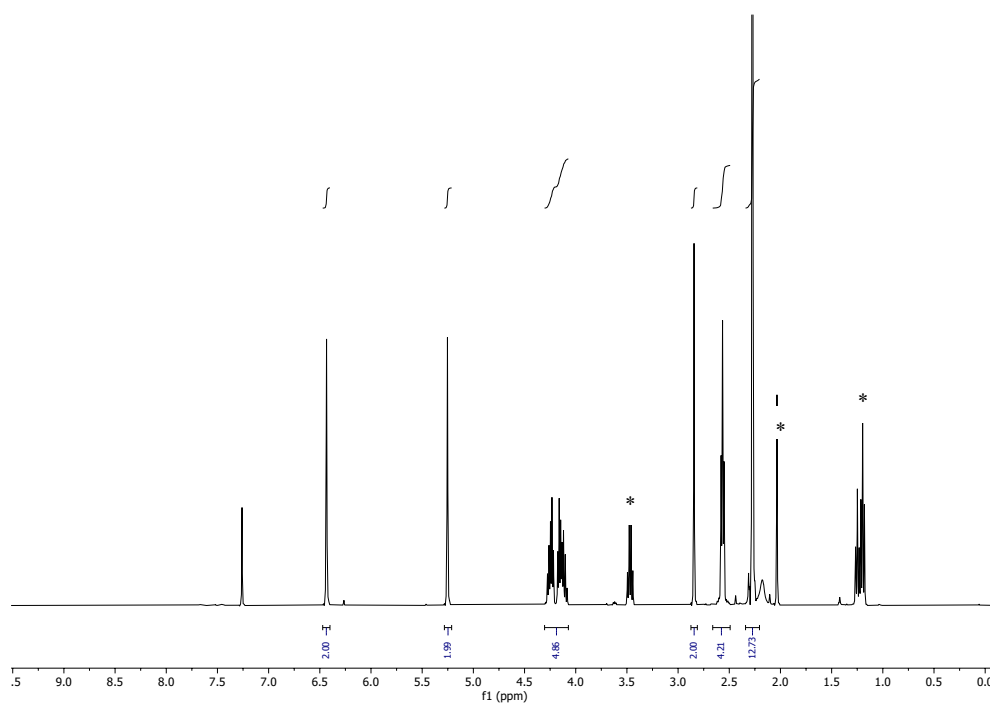


Figure S 6. ¹H NMR spectrum of **H**. CDCl₃, 400 MHz. *Residual ethyl acetate

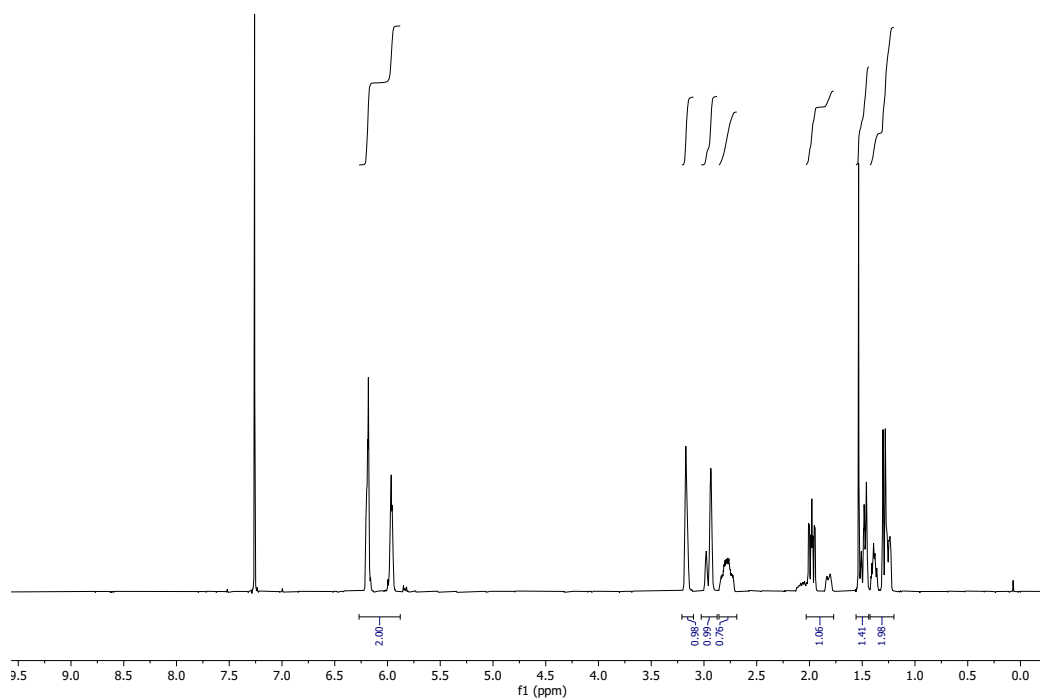


Figure S 7. ^1H NMR spectrum of **F**. CDCl_3 , 400 MHz.

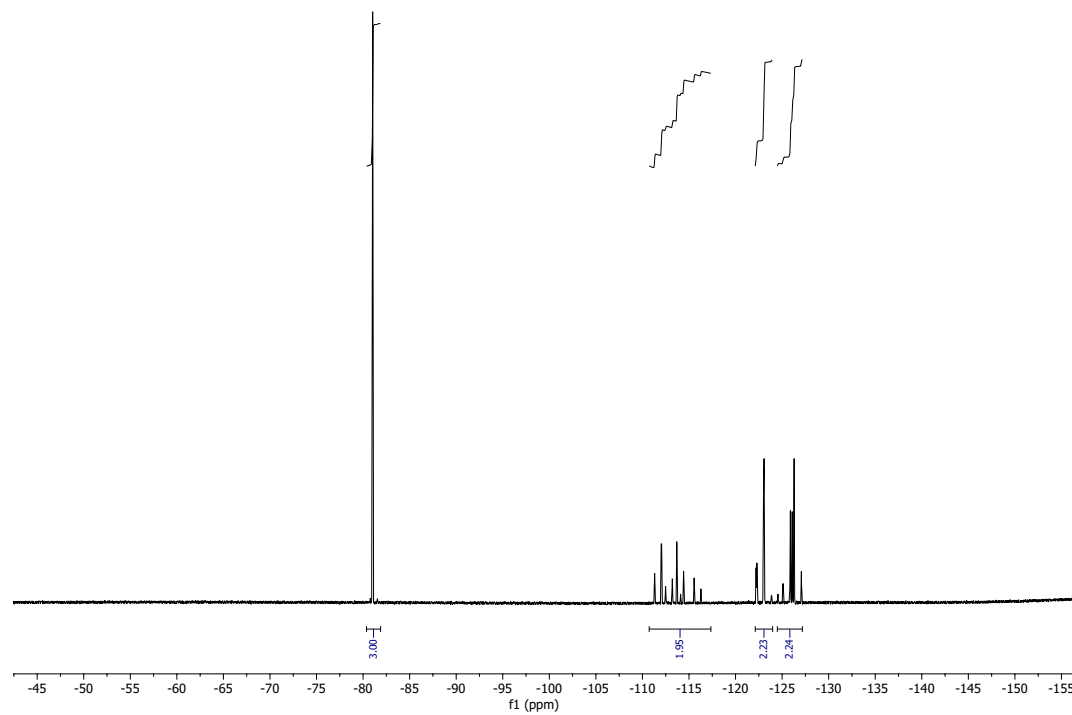


Figure S 8. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **F**. CDCl_3 , 376 MHz.

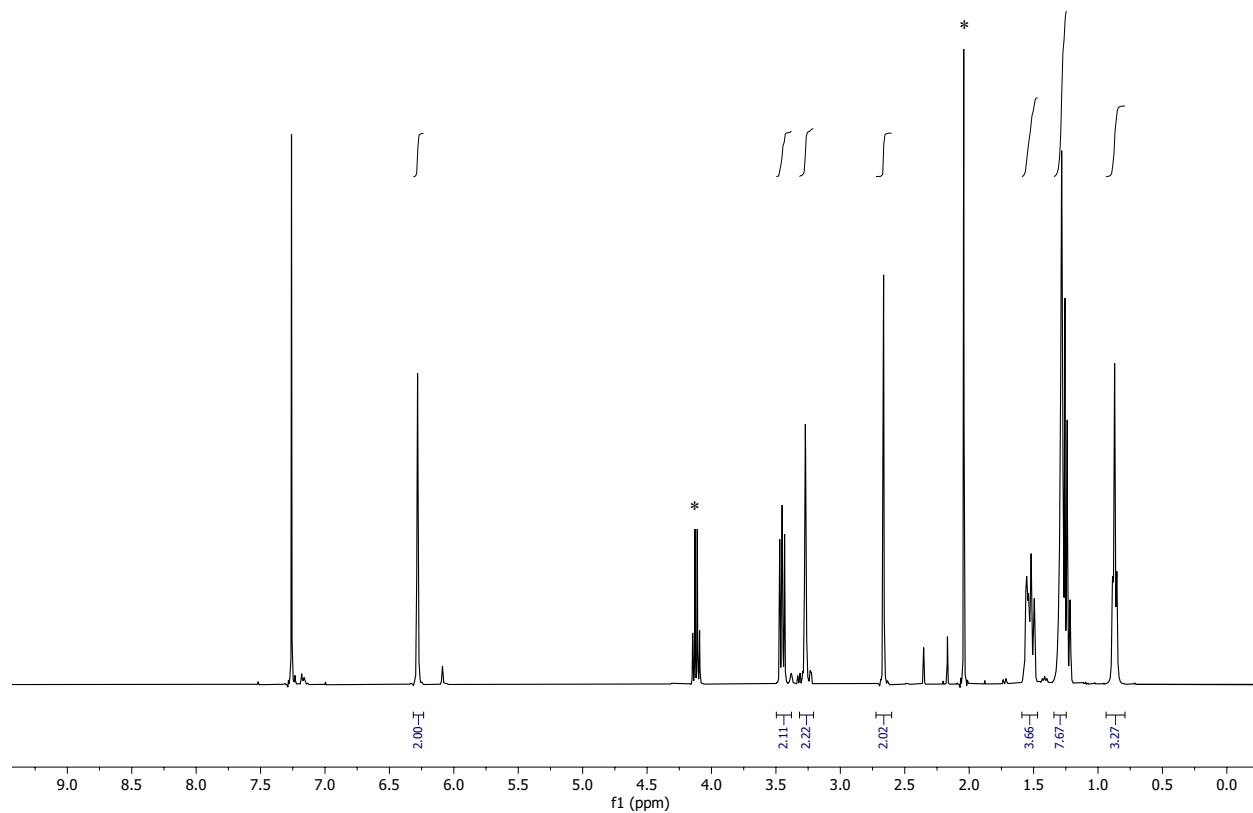


Figure S 9. ^1H NMR spectrum of **L**. CDCl_3 , 400 MHz. *Residual ethyl acetate

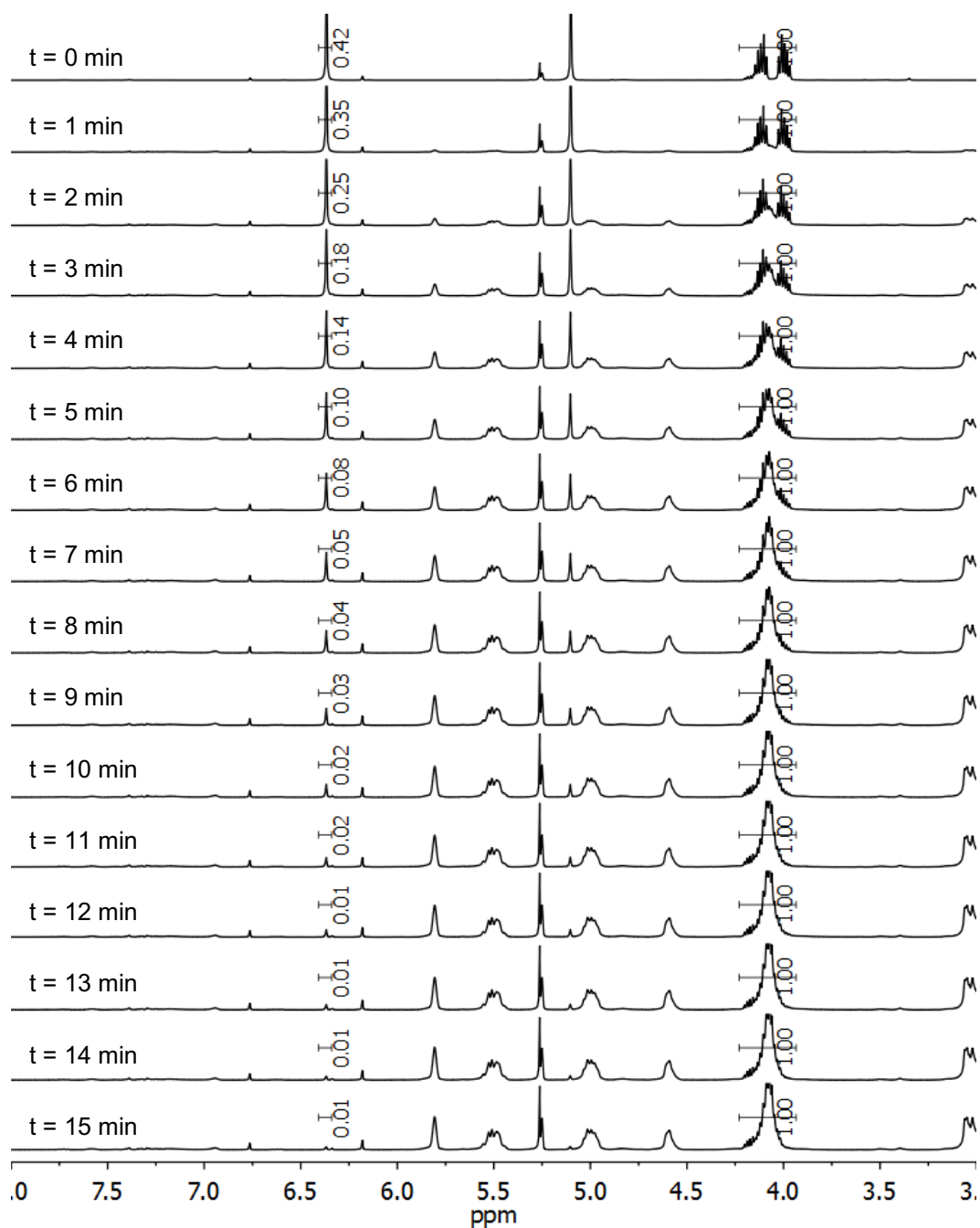


Figure S 10. Stacked ^1H NMR spectra of the ROMP of the hydrophilic monomer **H**. Integrals of the vinyl protons are compared to the $-\text{OCH}_2-$ protons.

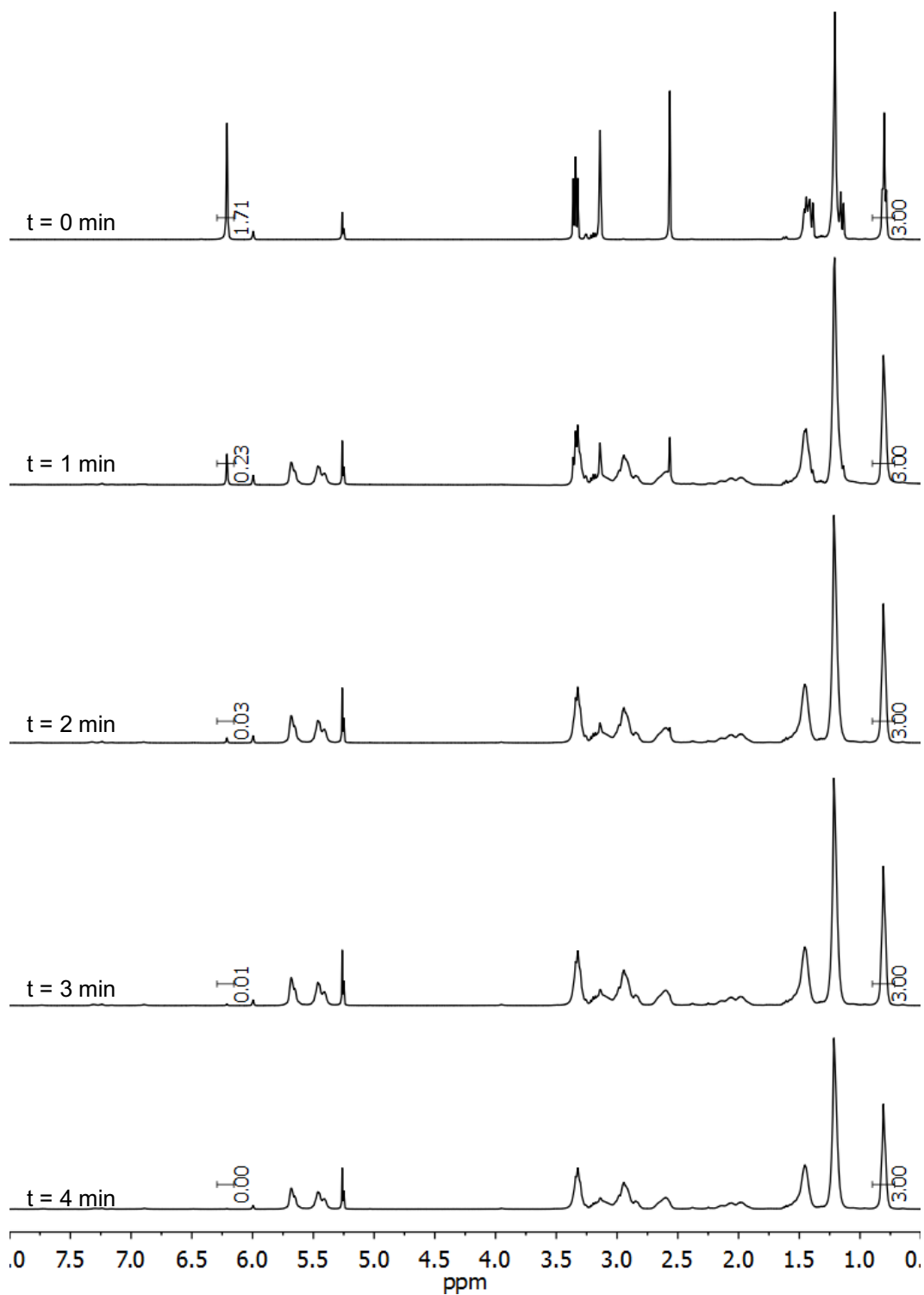


Figure S 11. Stacked ^1H NMR spectra of the ROMP of the lipophilic monomer **L**. Integrals of the vinyl protons are compared to the $-\text{CH}_3$ protons.

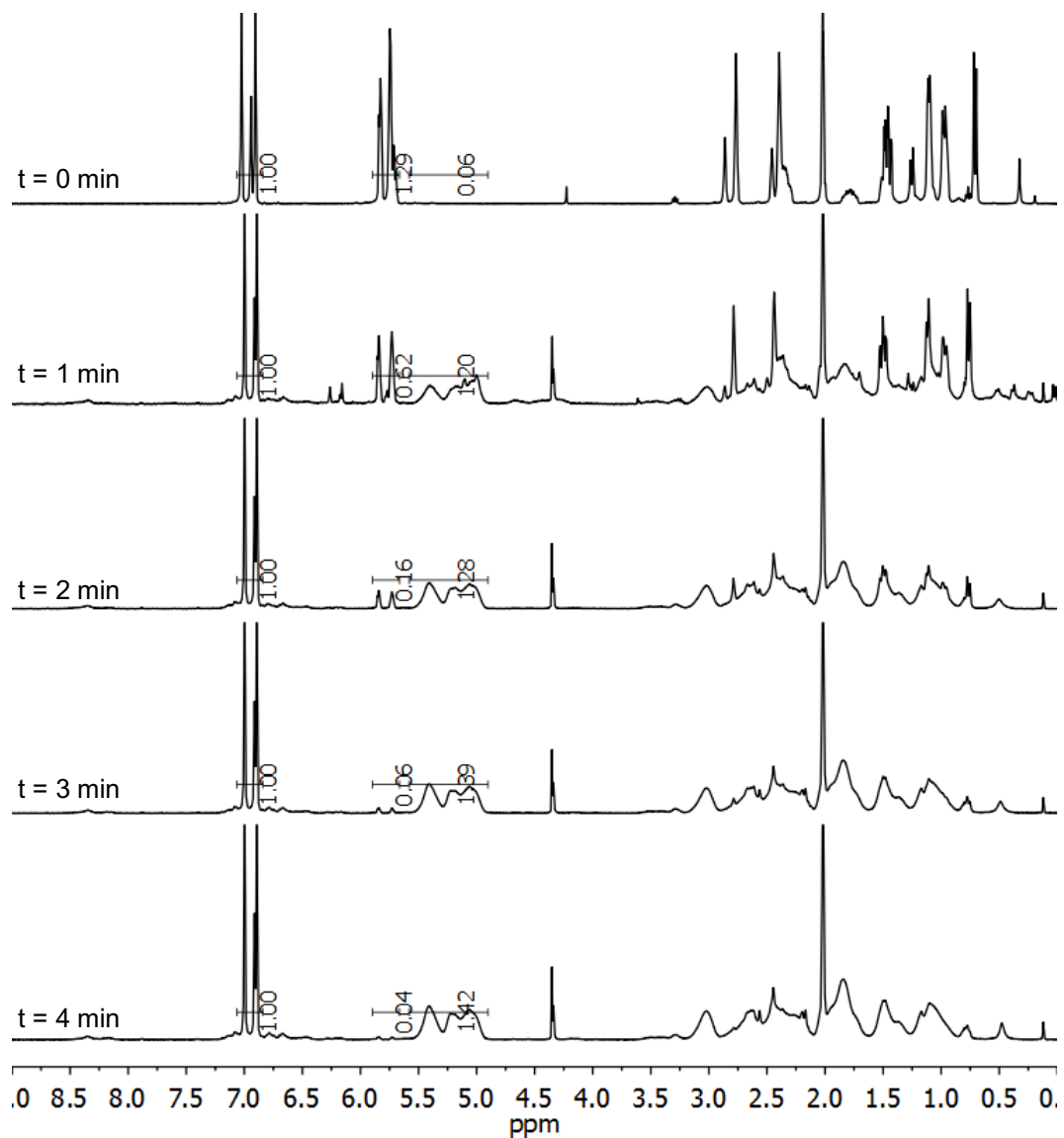


Figure S 12. Stacked ^1H NMR spectra of the ROMP of the fluorophilic monomer **F**. Integrals of the vinyl protons are compared to the residual protio solvent and the polymerized vinyl protons.

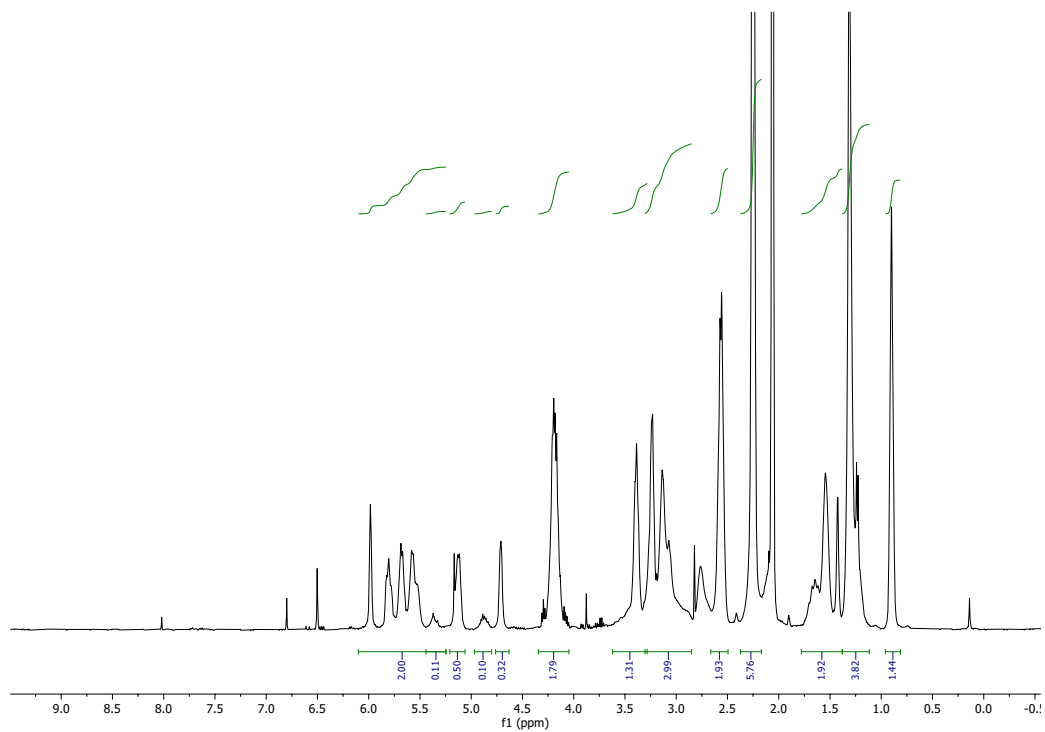


Figure S 13. Representative ^1H NMR spectrum of the triblock copolymer (Table 1, Series 2b). Acetone- d_6 , 600 MHz.

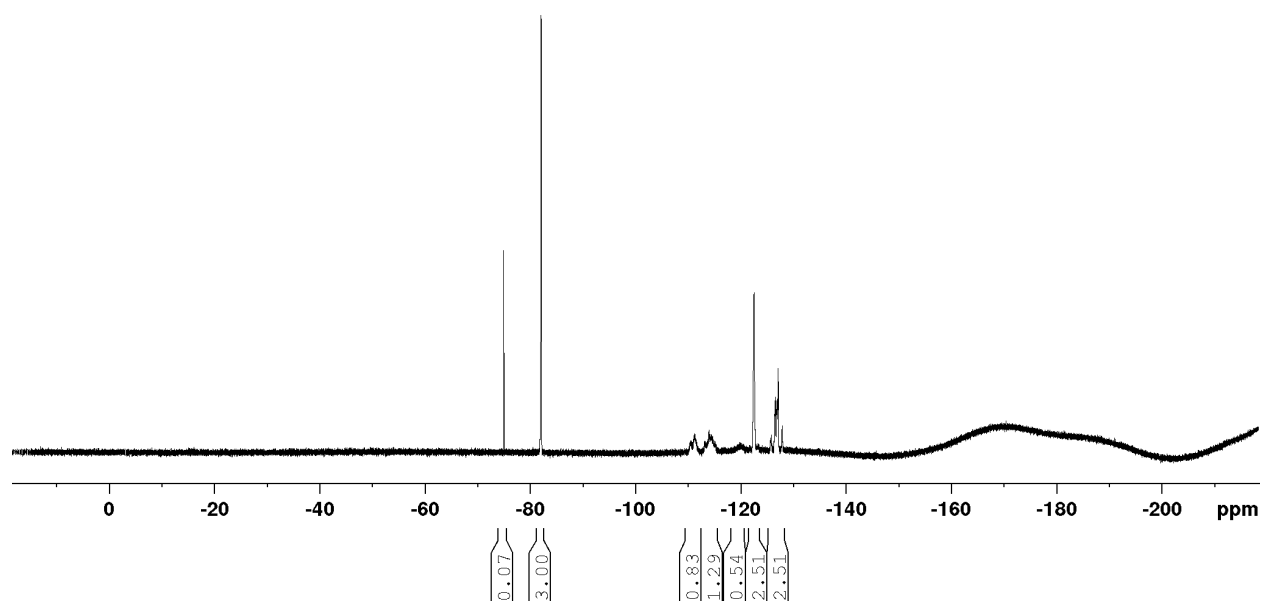


Figure S 14. Representative $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of triblock copolymer (Table 1, Series 2b). Acetone- d_6 , 376 MHz.

Gel-Permeation Chromatography Homopolymers

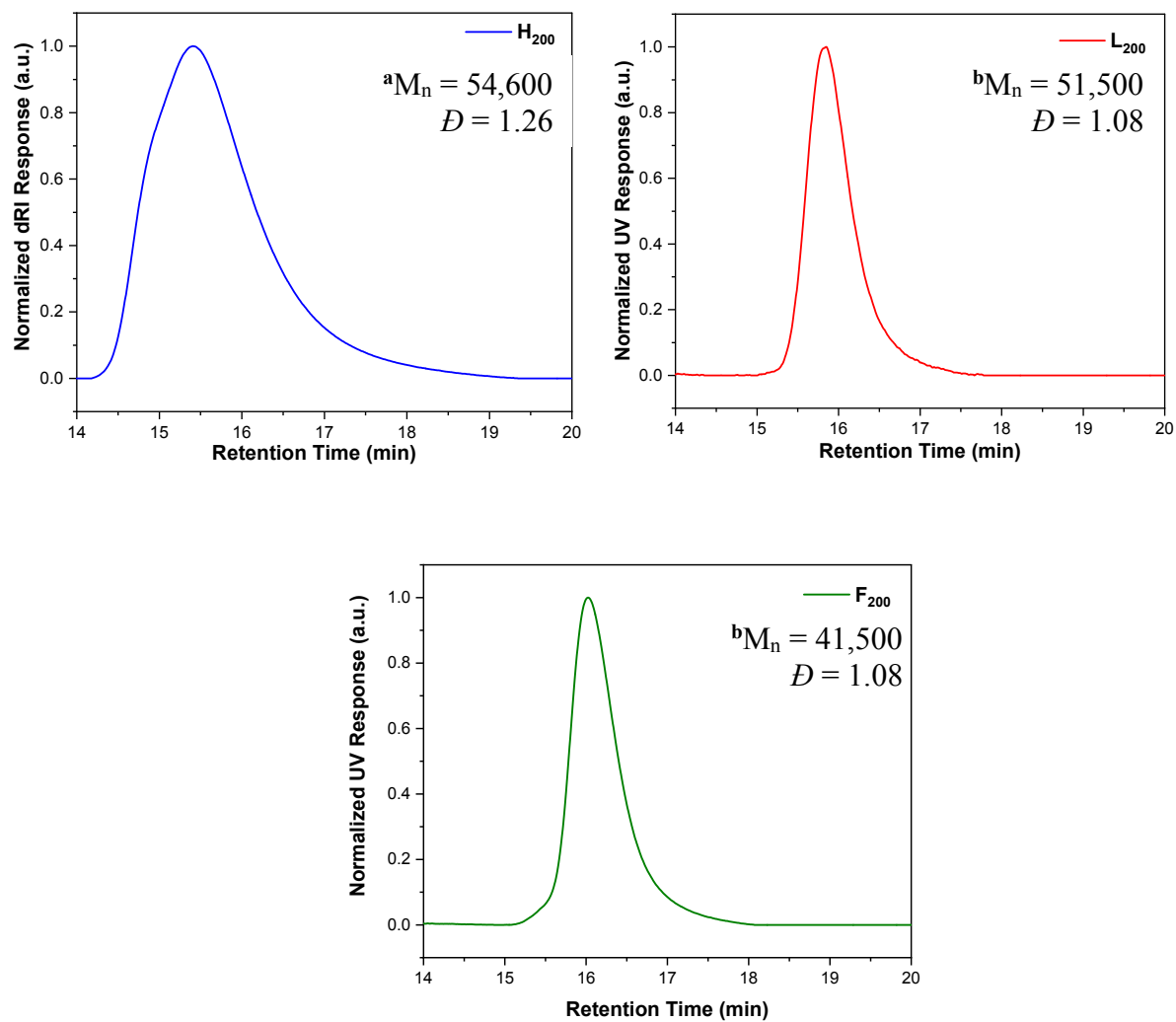


Figure S 15. GPC traces of each homopolymer. ^a 0.03 M LiCl solution in DMF as eluent; ^b THF as eluent.

Subsequent block incorporation

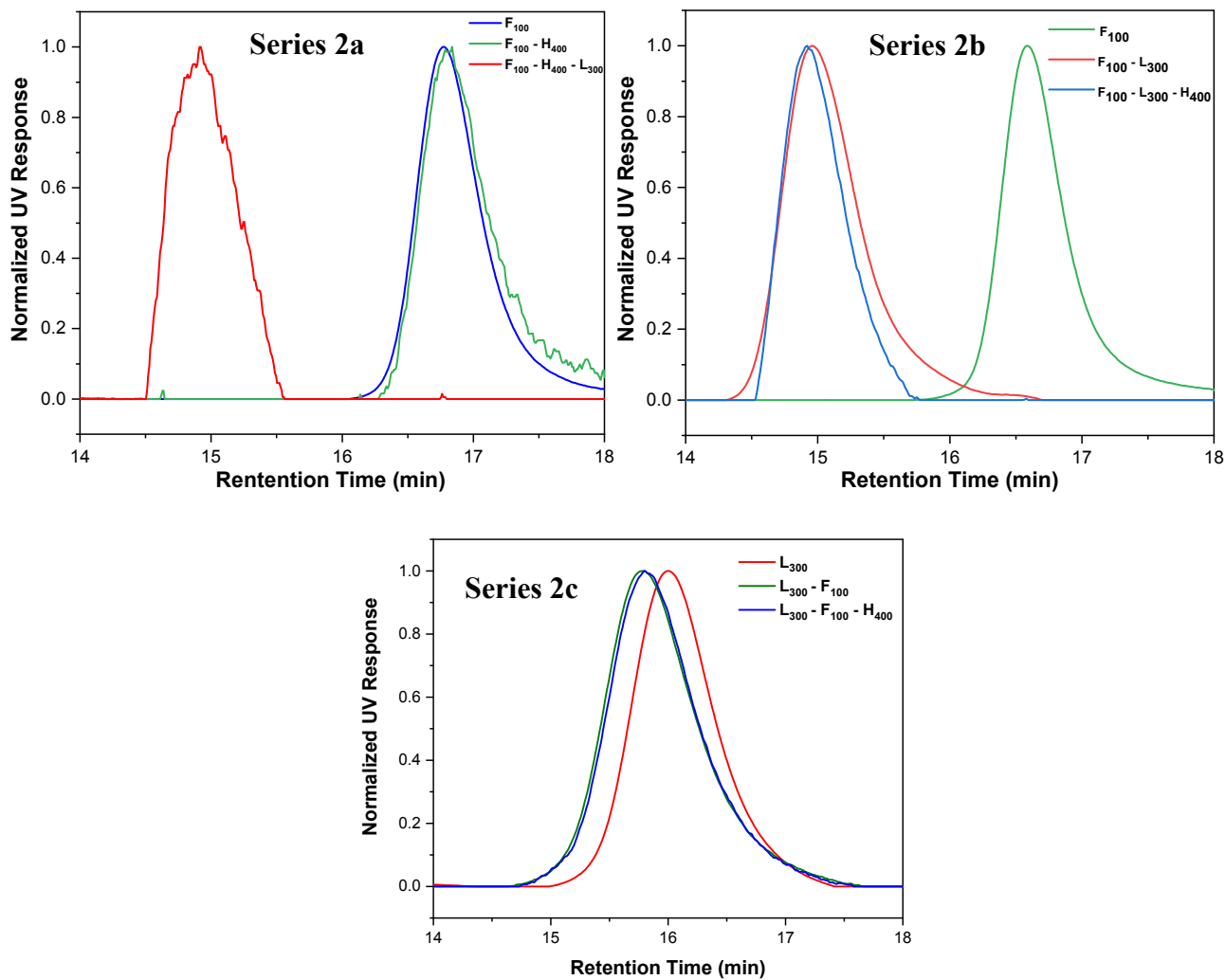
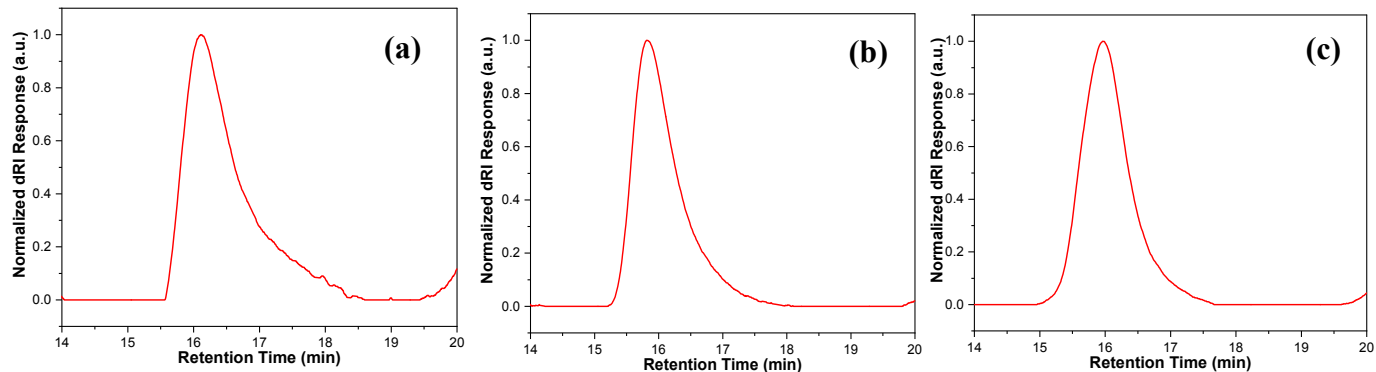


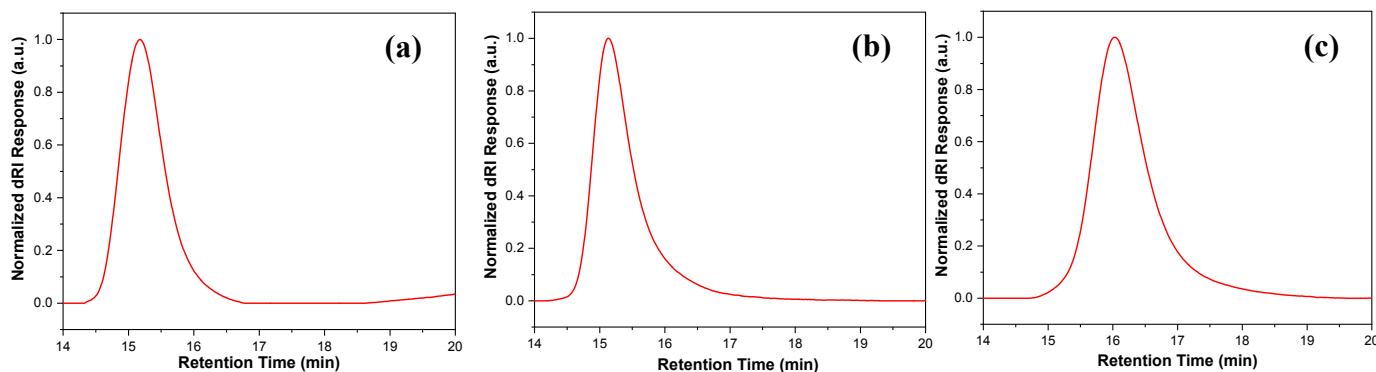
Figure S 16. Overlay of GPC traces for each monomer addition of **Series 2 a – 2 c** (Table S1, Series 2). The green trace corresponds to addition of **F**, the red trace corresponds to addition of **L**, and the blue trace corresponds to the addition of **H**.

Triblock terpolymers

Series 1:



Series 2:



Series 3:

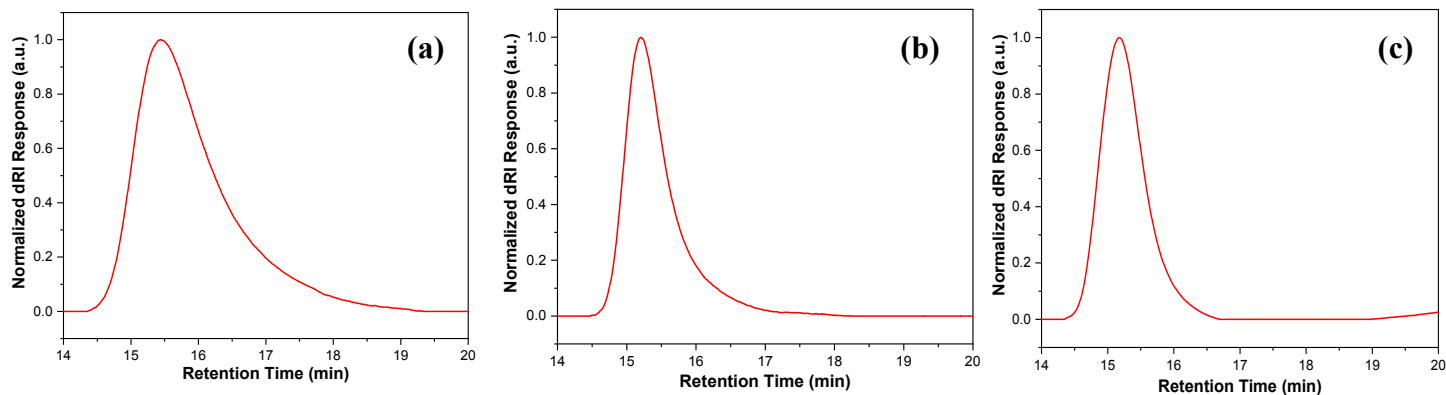


Figure S 17. GPC chromatograms of Triblock terpolymers using THF as the eluent. Entries correspond to the entries in Table S1, **Series 1 – 3** respectively.

Differential Scanning Calorimetry

Composition	T_g (°C)
F ₂₀₀	72
L ₂₀₀	91
F ₁₀₀ – H ₄₀₀ – L ₃₀₀	61; 94

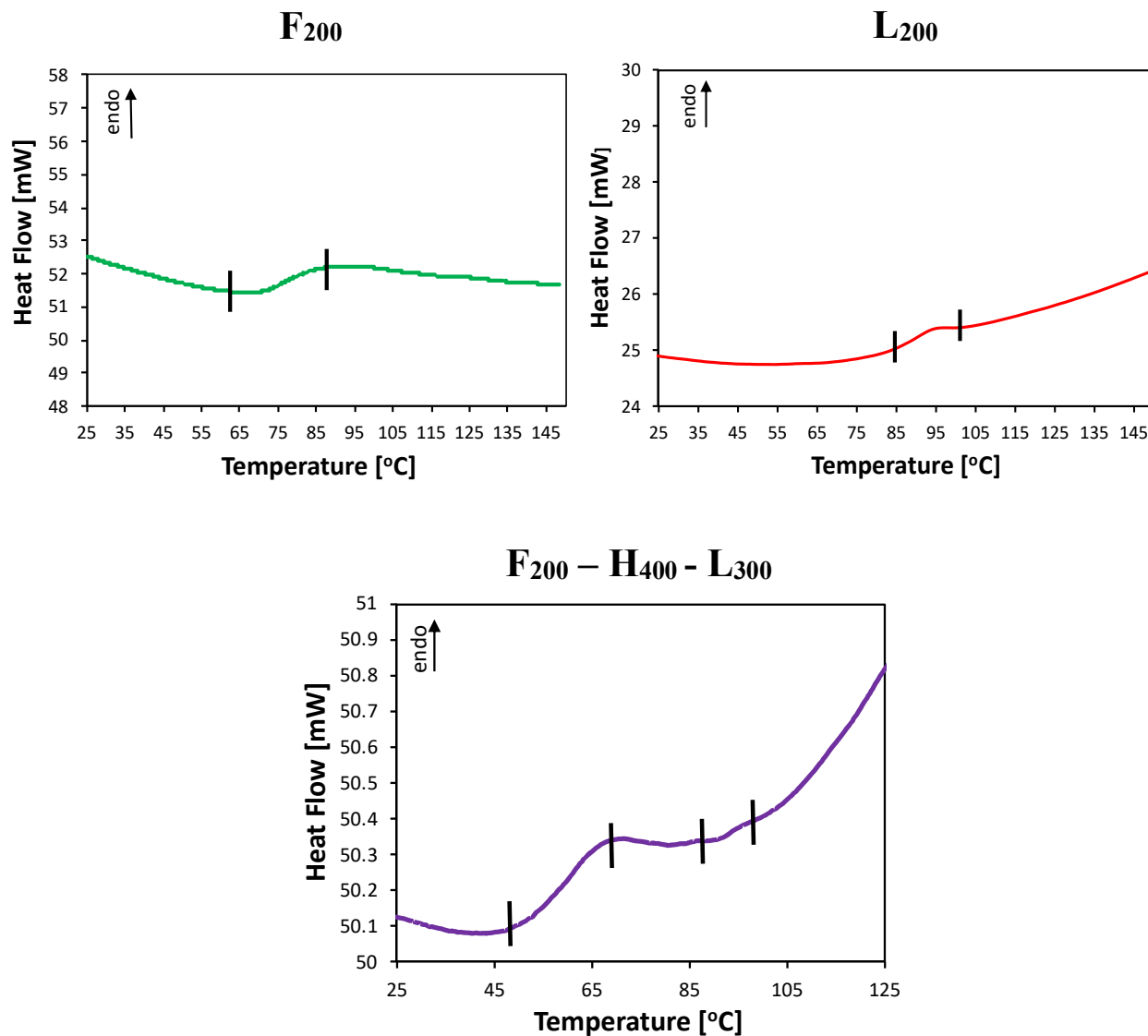


Figure S 18. DSC traces of homoblock and triblock copolymer to demonstrate block incorporation. The bars indicate the T_g .

Percent Composition Calculation

Percent calculation of the amount of **F**, **L**, and **H** in each triblock copolymer was calculated using the following equations:

$$\%F = \frac{A_F/0.71}{A_{tot}/2} \times 100 \quad \%L = \frac{A_L/3}{A_{tot}/2} \times 100 \quad \%H = \frac{A_H/4}{A_{tot}/2} \times 100$$

Where A_F is the integral between 5.43 – 5.23 ppm corresponding to the *cis* vinyl protons, A_L is the integral between 0.99 – 0.78 ppm corresponding to the $-\text{CH}_3$ protons, A_H is the integral between 4.26 – 4.07 ppm corresponding to the four $-\text{OCH}_2-$ protons, and A_{tot} is the integral between 6.04 – 5.23 ppm corresponding to the total vinyl protons. The normalization factor of 0.71 was determined from the ratio of *cis/trans* vinyl protons in the homopolymer ^1H NMR spectrum for **F** (assuming that the ratio of *cis/trans* is 50/50).

Dynamic Light Scattering Analysis

Procedure for micelle formation

10 mg of polymer was dissolved in 1 mL of acetone to obtain a solution with a concentration of 10 mg/mL. The solution was placed in a 1 kD dialysis bag and the solvent was exchanged with water by placing the dialysis bag in water. Dialysis water was replaced daily for one week to induce micelle assembly. After one week, the solution from the dialysis bag was passed through a 0.45 μm syringe filter and analyzed by DLS and Cryo-TEM.

Table S 1. Summary of particle sizes obtained by DLS.

(I) Diblock copolymers

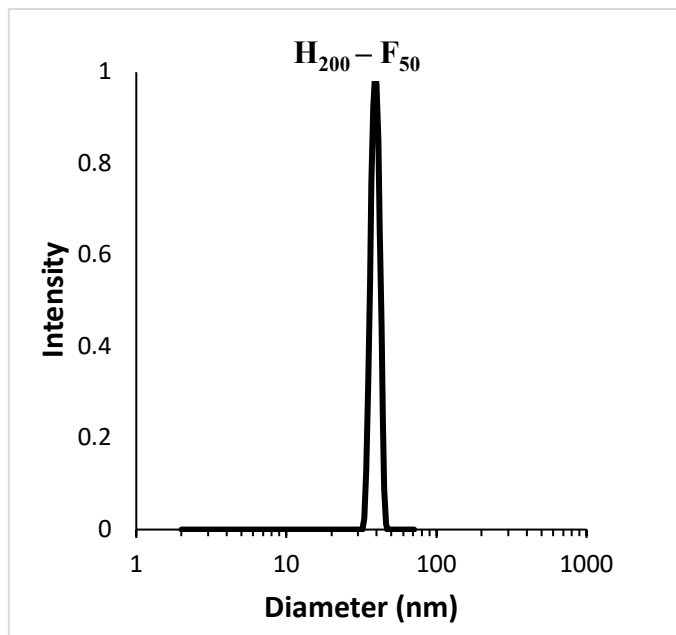
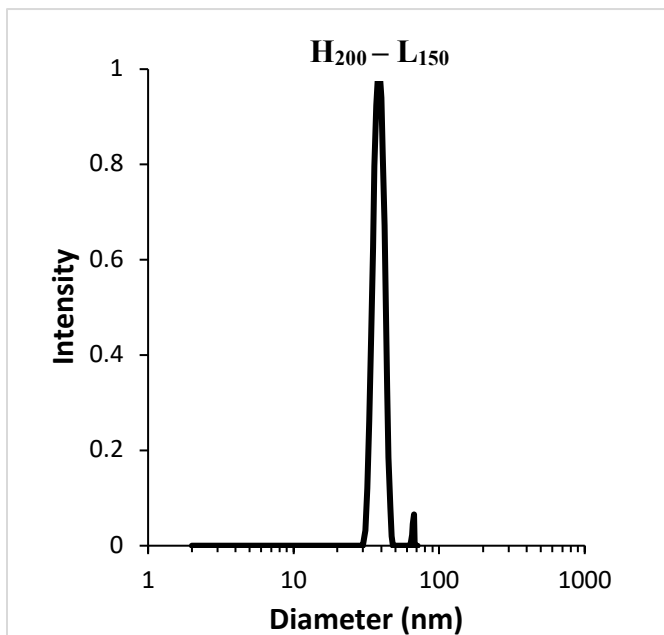
Composition	D _h , avg (nm)	PDI
H ₂₀₀ - L ₁₅₀	82	0.23
H ₂₀₀ - F ₅₀	86	0.16

(II) Triblock terpolymers

Series	Entry	Composition	D _h , avg (nm)	PDI
1 F _{0.4} - L _{0.6} - H ₁	a	F ₇₅ - H ₂₀₀ - L ₁₂₅	76	0.29
	b	F ₇₅ - L ₁₂₅ - H ₂₀₀	62	0.21
	c	L ₁₂₅ - F ₇₅ - H ₂₀₀	65	0.28
2 F _{0.25} - L _{0.75} - H ₁	a	F ₁₀₀ - H ₄₀₀ - L ₃₀₀	193	0.15
	b	F ₁₀₀ - L ₃₀₀ - H ₄₀₀	99	0.45
	c	L ₃₀₀ - F ₁₀₀ - H ₄₀₀	144	0.56
3 F _{0.3} - L ₁ - H _{0.8}	a	F ₁₂₅ - H ₃₀₀ - L ₃₇₅	136	0.21
	b	F ₁₂₅ - L ₃₇₅ - H ₃₀₀	242	0.01
	c	L ₃₇₅ - F ₁₂₅ - H ₃₀₀	170	0.32

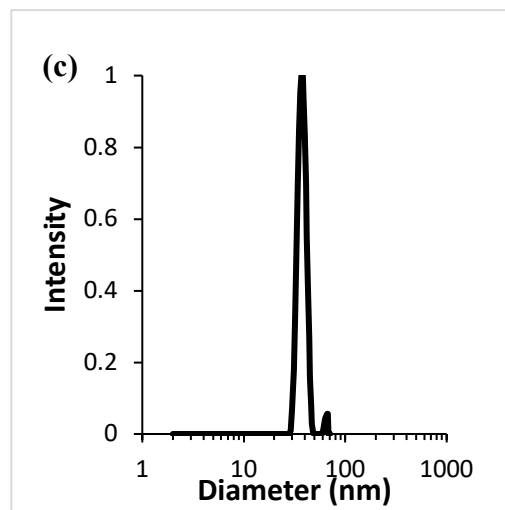
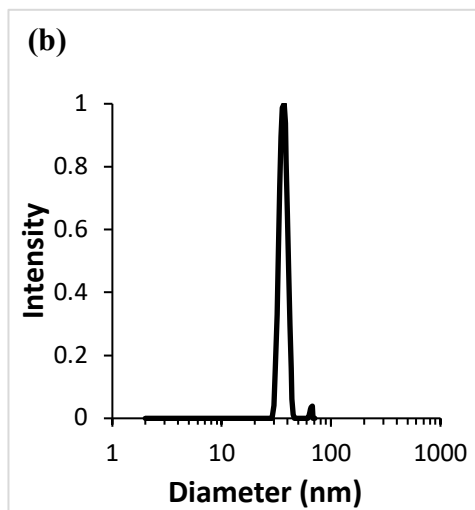
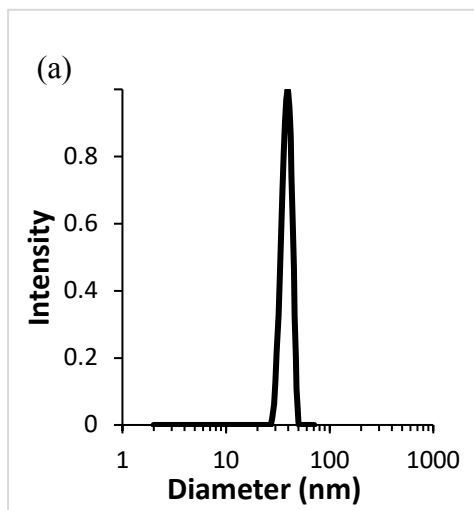
Particle Size Distributions by DLS

(I) Diblock copolymers

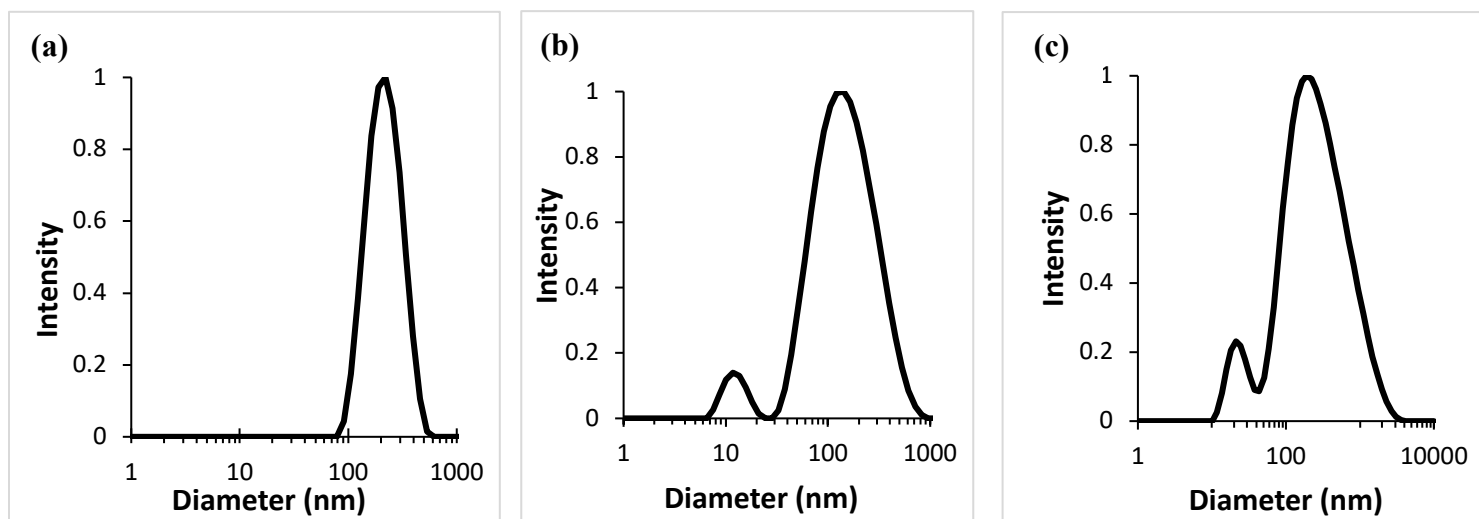


(II) Triblock terpolymers

Series 1:



Series 2:



Series 3:

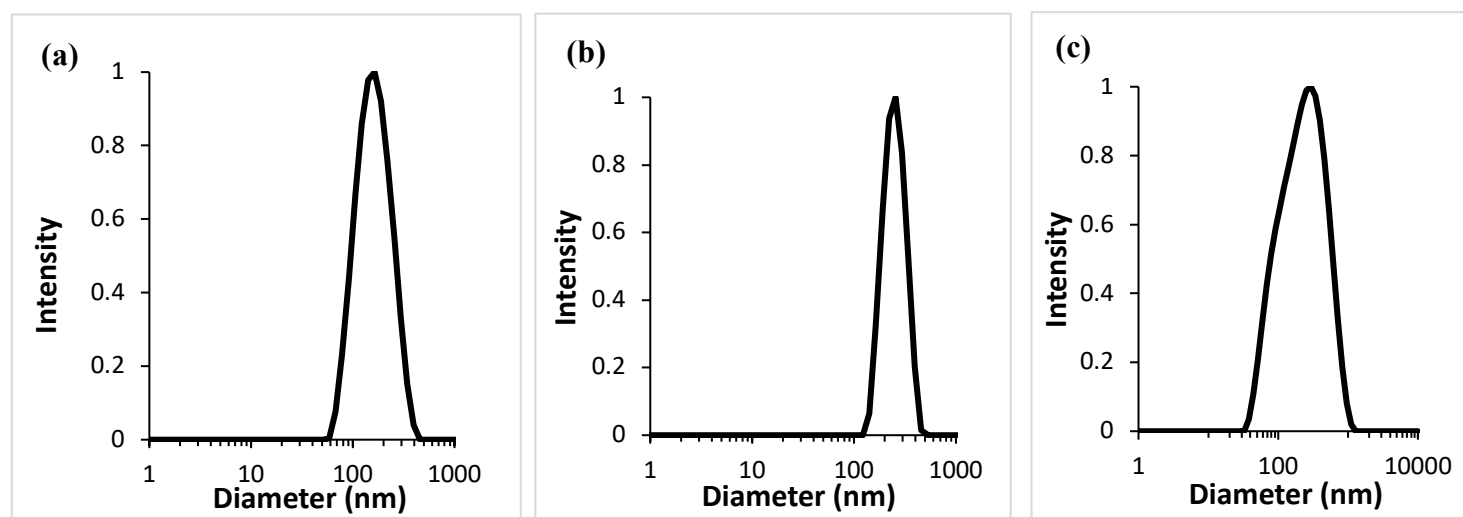


Figure S 19. DLS traces of self-assembled (I) Diblock copolymers (II) Triblock terpolymers in water. Samples were measured at a polymer concentration of 10 mg/mL.

Cryogenic Transmission Electron Microscopy

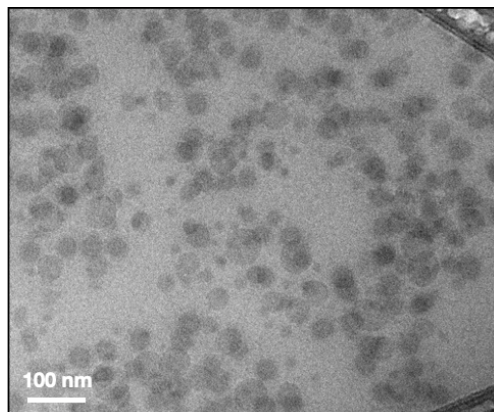


Figure S 20. Cryo-TEM micrograph of assembled nanostructures using $F_{100}-H_{200}-L_{100}$.

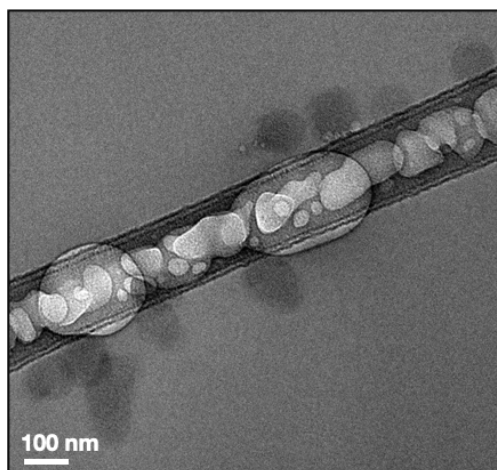


Figure S 21. Cryo-TEM micrograph of assembled nanostructures using $F_{150}-H_{200}-L_{100}$.

References

- (1) Sanford, M. S.; Love, J. A.; Grubbs, R. H. A Versatile Precursor for the Synthesis of New Ruthenium Olefin Metathesis Catalysts. *Organometallics* **2001**, *20*, 5314–5318.
- (2) Chae, C.-G.; Yu, Y.-G.; Seo, H.-B.; Kim, M.-J.; Grubbs, R. H.; Lee, J.-S. Experimental Formulation of Photonic Crystal Properties for Hierarchically Self-Assembled POSS–Bottlebrush Block Copolymers. *Macromolecules* **2018**, *51*, 3458–3466.
- (3) Yang, B.; Abel, B. A.; McCormick, C. L.; Storey, R. F. Synthesis of Polyisobutylene Bottlebrush Polymers via Ring-Opening Metathesis Polymerization. *Macromolecules* **2017**, *50*, 7458–7467.
- (4) Kim, K. O.; Choi, T.-L. Synthesis of Dendronized Polymers via Macromonomer Approach by Living ROMP and Their Characterization: From Rod-Like Homopolymers to Block and Gradient Copolymers. *Macromolecules* **2013**, *46*, 5905–5914.
- (5) Faulkner, C. J.; Fischer, R. E.; Jennings, G. K. Surface-Initiated Polymerization of 5-(Perfluoro-n-Alkyl)Norbornenes from Gold Substrates. *Macromolecules* **2010**, *43*, 1203–1209.
- (6) Perez, E.; Laval, J. P.; Bon, M.; Rico, I.; Lattes, A. Synthesis of Bicyclo [2· 2· 1] Hept-2-Enes with Mono and Disubstituted Long Perfluorinated Chains C_nF_{2n+1} ($n = 4,6,8,10$) Investigation of Association in Solution by ^{19}F NMR Study of Polymerization via a Metathetic Reaction. *J. Fluor. Chem.* **1988**, *39*, 173–196.
- (7) Alfred, S. F.; Lienkamp, K.; Madkour, A. E.; Tew, G. N. Water-Soluble ROMP Polymers from Amine-Functionalized Norbornenes. *J. Polym. Sci. A: Polym. Chem.* **2008**, *46*, 6672–6676.