General Methods

All reagents were purchased from commercial sources and used without further purification. Peptides were synthesized using an AAPPTEC Focus XC automated synthesizer. Amino acids were purchased from AAPPTEC and NovaBiochem. *N*-(Glycine)-*cis*-5-nrbornene-*exo*-dicarboximide, (1) $(IMesH_2)(C_5H_5N)_2(Cl)_2Ru{=}CHPh$ (2) and *N*-(hexanoic acid)-*cis*-5-norbornene-*exo*-dicarboximide were prepared according to published protocols. (3) All polymerizations were set up in J. Young NMR tubes (5 mm diameter) in a glove box under a dinitrogen atmosphere using DMF-d_7 drawn from sealed ampules (Cambridge Isoptopes). Trypsin was purchased from Gibco. All enzymatic reactions were done in 25 mM Tris buffer at pH 7.2 with 50 mM $CaCl_2$ and 150 mM NaCl. HPLC analysis was performed on a Jupiter Proteo90A phenomenex column (150 x 4.60 mm) using a Hitachi-Elite LaChrom L-2130 pump equipped with a UV-Vis detector (Hitachi-Elite LaChrome L-2420). Purification was done using a Jupiter Proteo90A Phenomenex column (2050 x 25.0 mm) on a Waters DeltaPrep 300 system. Buffer A was 0.1% TFA in water and Buffer B was 99.9% ACN and 0.1% TFA. The sequence identities of purified peptide-monomers were confirmed using ESI-MS in the UCSD Chemistry and Biochemistry Molecular Mass Spectrometry Facility. Polymer dispersities and molecular weights were determined by size-exclusion chromatography (phenomenex Phenogel 5u 10, 1k-75k, 300 x7.80 mm in series with a Phenomex Phenogel 5u 10, 10K-1000K, 300 x 7.80 mm (0.05 M LiBr in DMF)) using a Shimadzu pump equipped with a multi-angle light scattering detector (DAWN-HELIOS: Wyatt Technology) and a refractive index detector (Hitachi L-2490) normalized to a 30,000 MW polystyrene standard. In the situations where a multimodal distribution is observed by light scattering but not in the RI chromatogram, we analyzed only the peak width that has an associated RI component (*i.e.* S4 d). ^1H (400 MHz) NMR spectra were

recorded on a Varian Mercury Plus spectrometer. Chemical shifts were reported in ppm relative to the DMF residual proton peaks.

Peptide Synthesis

Peptide monomers 1-31 and monomers for figures S37-S40 were synthesized via standard FMOC-based solid phase synthesis using Rink Amide MBHA resin (AAPPTEC) via automated synthesis. In brief, FMOC deprotection was performed using 20% 4-methylpiperidine in DMF. Amino acid couplings were carried out using HBTU and DIPEA (resin/amino acid/HBTU/DIPEA 1:3.5:3.4:4). The final peptide monomers were cleaved from the resin using a mixture of TFA/H2O/TIPS (95:2.5:2.5) for 45 minutes. The peptides were precipitated and washed with cold ether. The peptides were dissolved in buffer A with minimal amounts of buffer B. Peptides were analyzed using RP-HPLC and purified using preparative HPLC. Peptide identity and purities were confirmed using ESI-MS and RP-HPLC monitoring at l_{abs} = 214 nm. Peptide monomers for figures S32-S34 and was synthesized via standard FMOC-based solid phase synthesis using Sieber Amide Resin (AAPPTEC). Standard solid phase peptide synthesis protocols were followed for the preparation of the side-chain protected monomers with the following exceptions. The resin was swelled for 1 hr in DMF and then the initial N-terminal FMOC protecting group was removed by shaking in a solution of 20% 4-methylpiperidine in DMF for 5 min and then again for 1 hr. The initial amino acid was loaded onto the resin for 1 hr, the solution was drained and then a fresh set of amino acid/coupling agent was added and mixed for 1 hr to ensure complete loading. Peptides were cleaved from the resin using 2% TFA in DCM for 45 minutes. The peptides were precipitated and washed with cold ether. The peptides were dissolved in buffer A with minimal amounts of buffer B. Peptides were analyzed using RP-HPLC and purified using preparative

HPLC. Peptide identity and purities were confirmed using ESI-MS and RP-HPLC monitoring at l_{abs} = 214 nm.

Polymer synthesis

The peptide monomers were polymerized via ROMP using Grubbs' modified second generation catalyst [$(H_2IMES)(pyr)_2(Cl)_2Ru$=CHPh]. The catalyst (1 equiv) was dissolved in DMF-d_7 and added to peptide-norbornene monomer (20 or 200 equiv) in DMF-d_7 to a final volume of 500 μL in a J. Young NMR tube under inert environment. The resulting mixture was monitored by NMR and checked for completion at 1 hour, 2 hours, 3 hours and 24 hours. Once complete, or at 24 hours, the polymerization was quenched with ethyl vinyl ether (2 equiv). The polymers were characterized via SEC-MALS.

Kinetic analysis of polymerization reactions

The peptide-modified monomer (0.006 mmol) was dissolved in 480 μL of DMF-d_7 and transferred to a J-Young NMR tube in a glove box. The tube was removed from the box and a ^{1}H NMR spectra (t = 0) was taken using eight scans with a 1s interval between scans to allow time for proton relaxation. The tube was returned to the glove box and the catalyst (0.0003 mmol) in 20 μL of DMF-d_7 was added to the reaction solution. ^{1}H NMR spectra were recorded at the indicated time points for up to 3 hours. If the proton resonance corresponding to the monomer olefin ($\delta \cong 6.3$ ppm) was still present after 3 hrs, then a final spectrum was recorded 24 hours after addition of the catalyst. Percent conversions were calculated from the integral values (polymer olefin)/(monomer olefin + polymer olefin) after subtracting the baseline integrals. Initial rates were obtained from a plot of $\ln([M_o]/[M_t])$ vs. time, where monomer concentration

was determined from the calculated percent conversion at each time point.

Deprotection of protecting groups from polymers

Following completion of polymerization, the side-chain protected polymers were precipitated with 10 mL of cold ether and collected by centrifugation. The resulting powder was washed with cold ether (×3), collected by centrifugation, and dried overnight under vacuum. The resulting white powder was dissolved in 2 mL of a mixture of TFA/H_2O/TIPS (95:2.5:2.5) and stirred for 4 hours at room temperature. The product was precipitated with cold ether, collected by centrifugation, dissolved in 1 mL of H_2O and then lyophilized overnight to yield a fluffy white powder. A comparison of ^{1}H NMR spectra before and after cleavage suggests complete removal of side-chain protecting groups (Figure S43).

Enzymatic studies

Polymers were prepared as in the main text experimental section, with removal of DMF under vacuum with toluene added. With a concentrated solution in DMF/toluene, the catalyst was removed by cold ether precipitation of the polymer. Residual ether was then removed under vacuum. Dry polymer was dissolved in Tris buffer to yield a 2 mM solution. Next, 20 mL of Trypsin (1 mM), 20 mL of monomer or polymer (2 mM), 20 mL Tris buffer (250 mM Tris pH 7.2, 1500 mM NaCl, 500 mM $CaCl_2$) and 140 mL of water were added to a HPLC vial and loaded in the autosampler carousel and a sample immediately taken for injection at 1 min. Subsequently, the reaction was monitored via RP-HPLC (10-80% buffer B) with an injection every 45 minutes following the initial injection.

Generating an HPLC standard curve for trypsin cleavage studies

Peptides were prepared to match the expected cleavage products from polymers of **33** and **34** (trypsin substrates, see main text): Gln-Leu-Ile-Ser-Gly-Ser-Gly-Ser and Gln-Leu-Ile-Ser. Purified peptides (see above) were dissolved to a final concentration of 1 mM in 10% buffer B (ACN in 0.1%TFA). Serial dilutions were made to give solutions with peptide concentrations of 500, 200, 100, 60, 40, and 20 mM. The peak area was determined in triplicate for each concentration of peptide using reverse phase HPLC from 10-80% buffer B to generate a standard curve of concentration against peak area (see Figure S38).

Standard SEC-MALS conditions

Phenomenex Phenogel 5u 10, 1k-75k, 300 x7.80 mm in series with a Phenomex Phenogel 5u 10, 10K-1000K, 300 x 7.80 mm (0.05 M LiBr in DMF)) using a Shimatzu pump equipped with a multi-angle light scattering detector (DAWN-HELIOS: Wyatt Technology) and a refractive index detector (Hitachi L-2490) normalized to a 30,000 MW polystyrene standard at a flow rate of 0.75 mL/min.

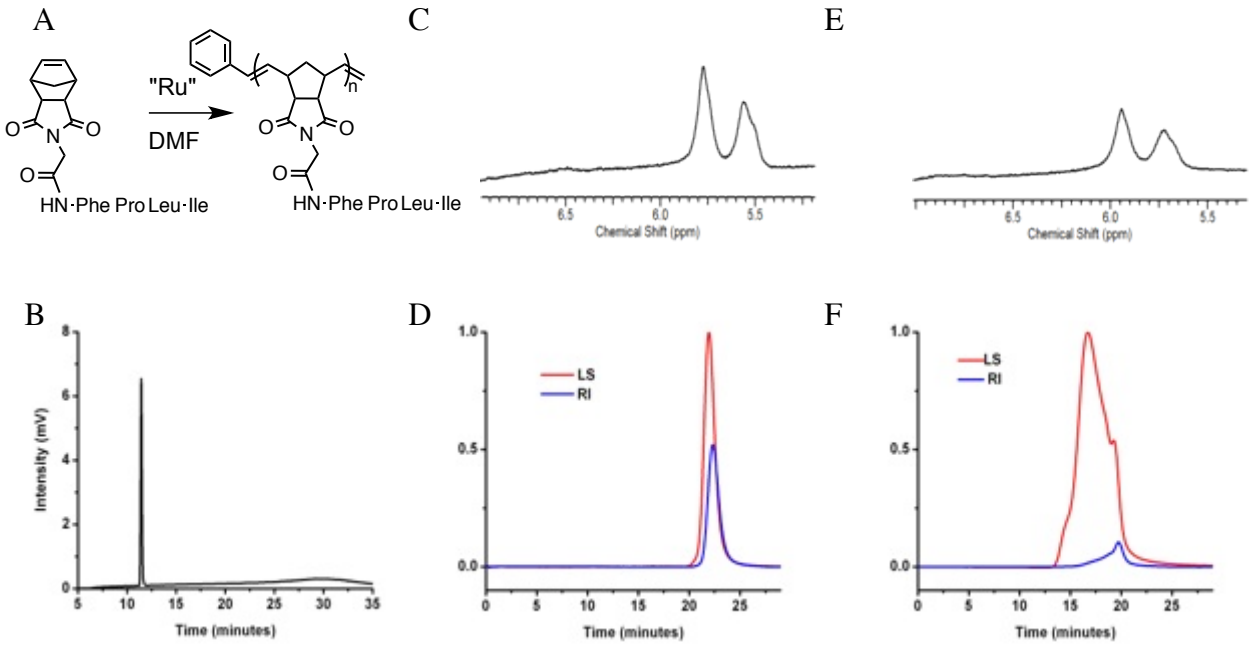


Fig. S1. Polymerization and analysis of $\mathbf{1}_{15}$ and $\mathbf{1}_{191}$

(A) Monomer and polymer structure: n = 15 or 191 (see Table 2, main text).
(B) RP-HPLC trace of **1** in 30-60% buffer B, retention time 12 minutes.
ESI-MS: Mass calc 690.31; Mass obs 691.4.
(C) ^{1}H NMR of **1** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data for polymer $\mathbf{1}_{15}$. SEC-MALS: M_n = 10,370 g/mol, PDI = 1.015.
(E) ^{1}H NMR of **1** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{1}_{191}$. SEC-MALS: M_n = 132,530 g/mol, PDI=1.045

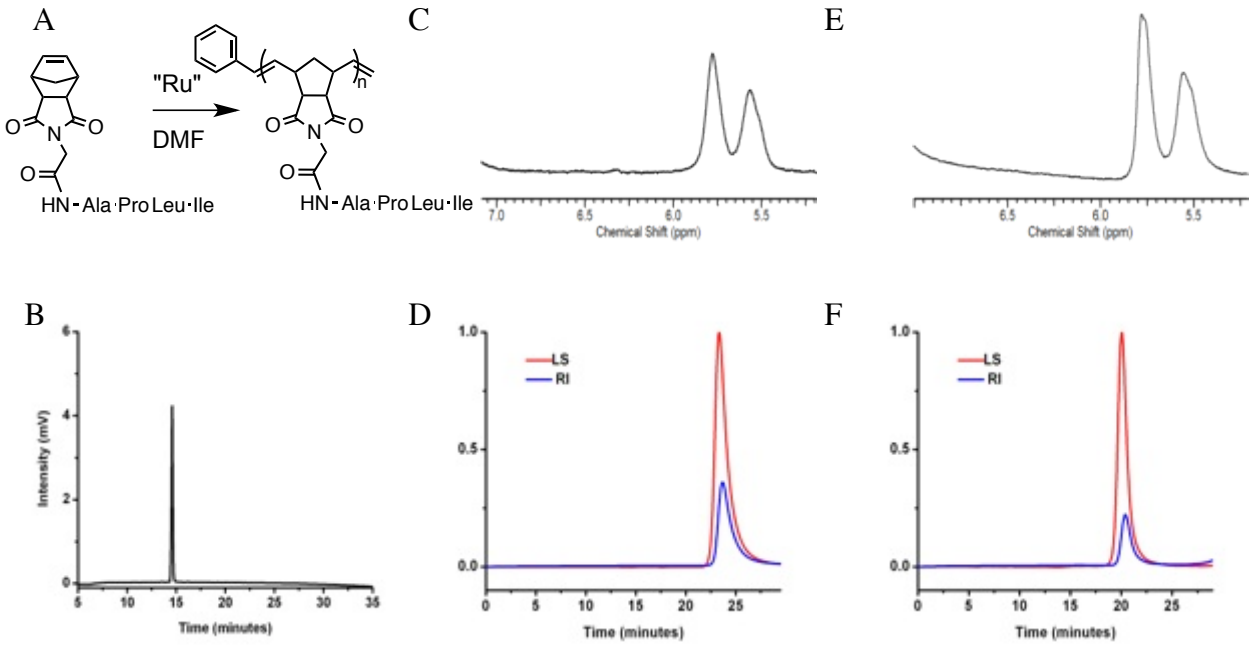


Fig. S2. Polymerization and analysis of $\mathbf{2}_{22}$ and $\mathbf{2}_{194}$

(A) Monomer and polymer structure: n = 22 or 194
(B) RP-HPLC trace of **2** in 35-55% buffer B, retention time 15 minutes.
ESI-MS: Mass calc 614.34; Mass obs 615.5
(C) ^{1}H NMR of **1** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{2}_{22}$. SEC-MALS: M_n = 13,920 g/mol, PDI = 1.027
(E) ^{1}H NMR of **1** following monomer polymerization: M:I = 20:1
(F) SEC-MALS data of polymer $\mathbf{2}_{194}$. SEC-MALS: M_n = 119,420 g/mol, PDI =1.024

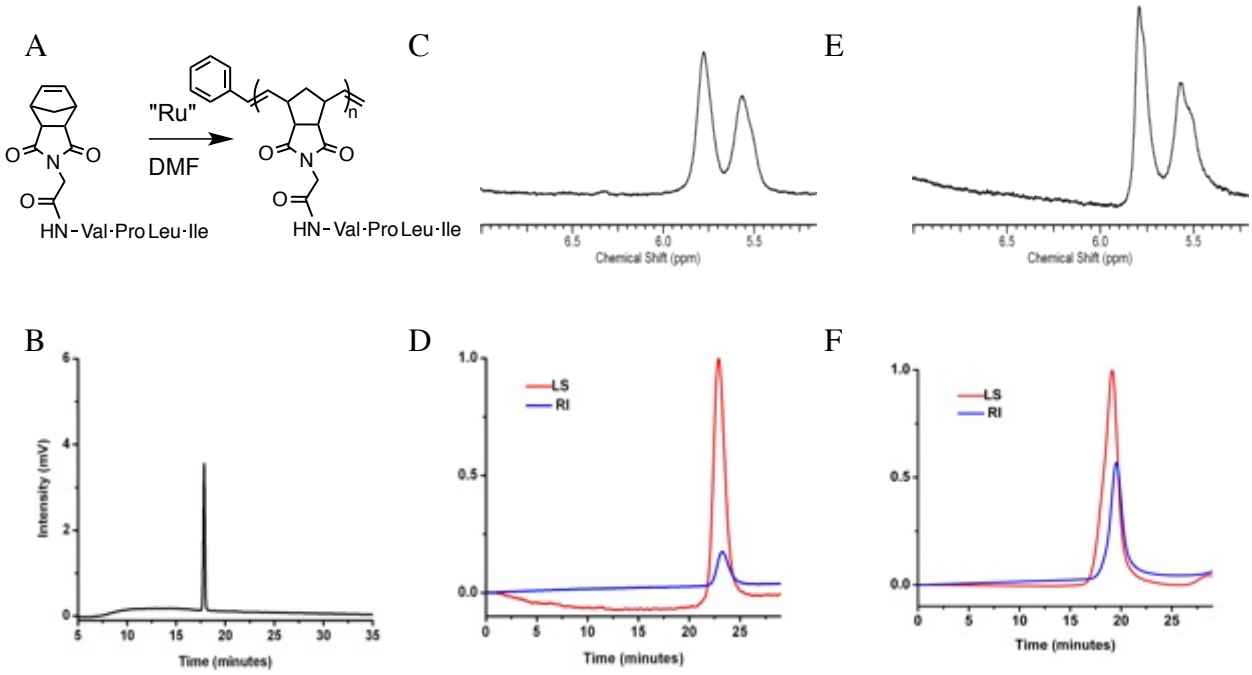


Fig. S3. Polymerization and analysis of $\mathbf{3}_{23}$ and $\mathbf{3}_{187}$

(A) Monomer and polymer structure: n = 23 or 187 (see Table 2, main text).
(B) RP-HPLC trace of **3** in 35-60% buffer B, retention time 18 minutes. ESI-MS: Mass calc 642.37; Mass obs 643.5
(C) ^{1}H NMR of **3** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{3}_{23}$. SEC-MALS: M_n = 14,310 g/mol, PDI = 1.060
(E) ^{1}H NMR of **3** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{3}_{187}$. SEC-MALS: M_n = 120,590 g/mol, PDI = 1.028

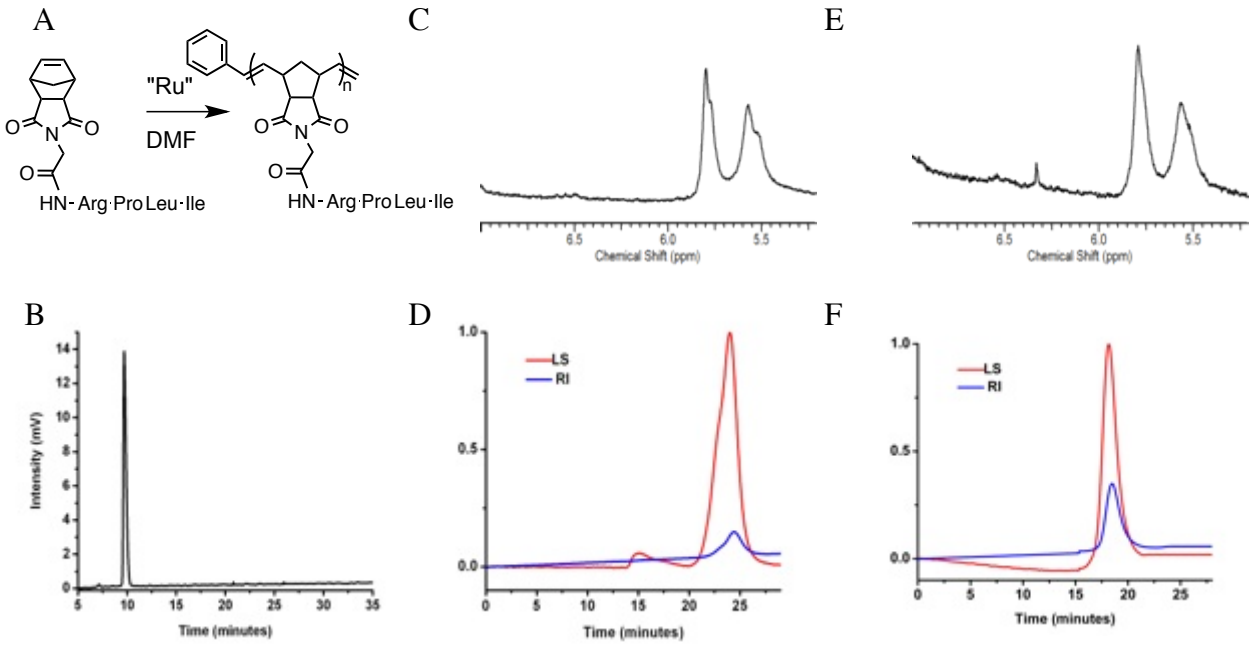


Fig. S4. Polymerization and analysis of $\mathbf{4}_{15}$ and $\mathbf{4}_{155}$.

(A) Monomer and polymer structure: n = 15 or 155 (see Table 2, main text).
(B) RP-HPLC trace of **4** in 30-50 % buffer B, retention time 10 minutes.
ESI-MS: Mass calc 699.41; Mass obs 700.64
(C) ^{1}H NMR of **4** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{4}_{15}$. SEC-MALS: M_n = 10,690 g/mol, PDI = 1.102
(E) ^{1}H NMR of **4** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{4}_{155}$. SEC-MALS: M_n = 108,400 g/mol, PDI = 1.087

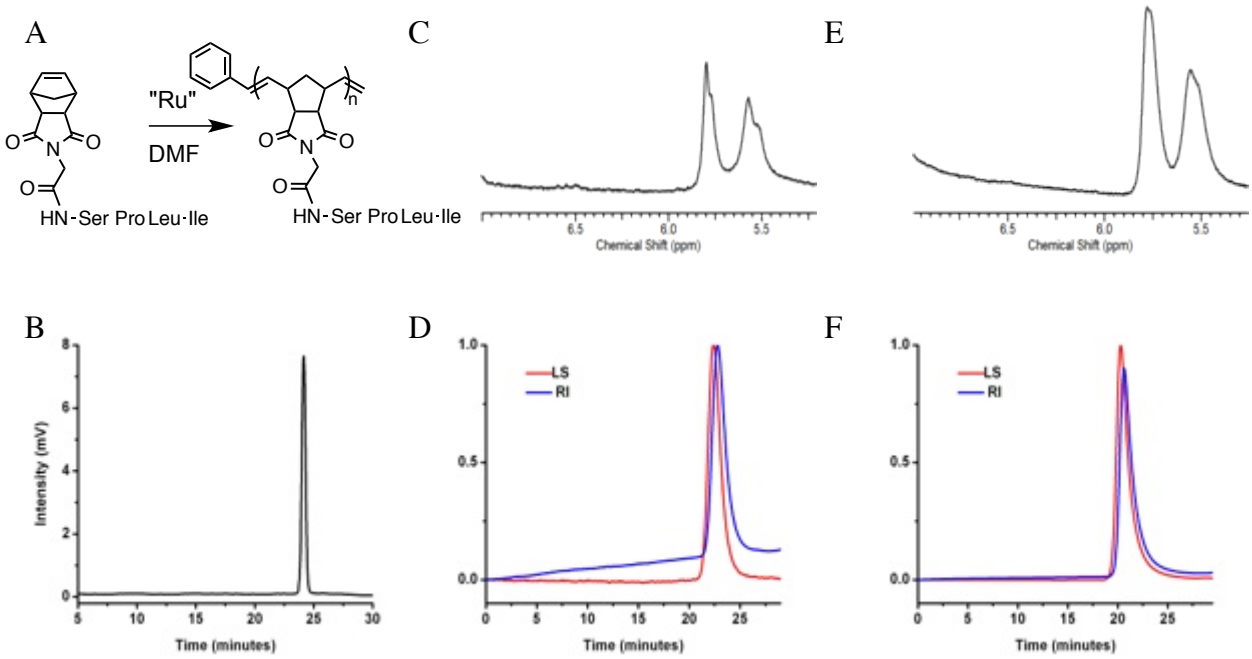


Fig. S5. Polymerization and analysis of $\mathbf{5}_{23}$ and $\mathbf{5}_{125}$

(A) Monomer and polymer structure: n=23 or 125.
(B) RP-HPLC trace of **5** in 25-45 % buffer B, retention time 24 minutes.
ESI-MS: Mass calc 630.73; Mass obs 631.64
(C) ^{1}H NMR of **5** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{5}_{23}$. SEC-MALS: M_n = 14,670 g/mol, PDI = 1.022
(E) ^{1}H NMR of **5** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{5}_{125}$. SEC-MALS: M_n = 78,950 g/mol, PDI = 1.008

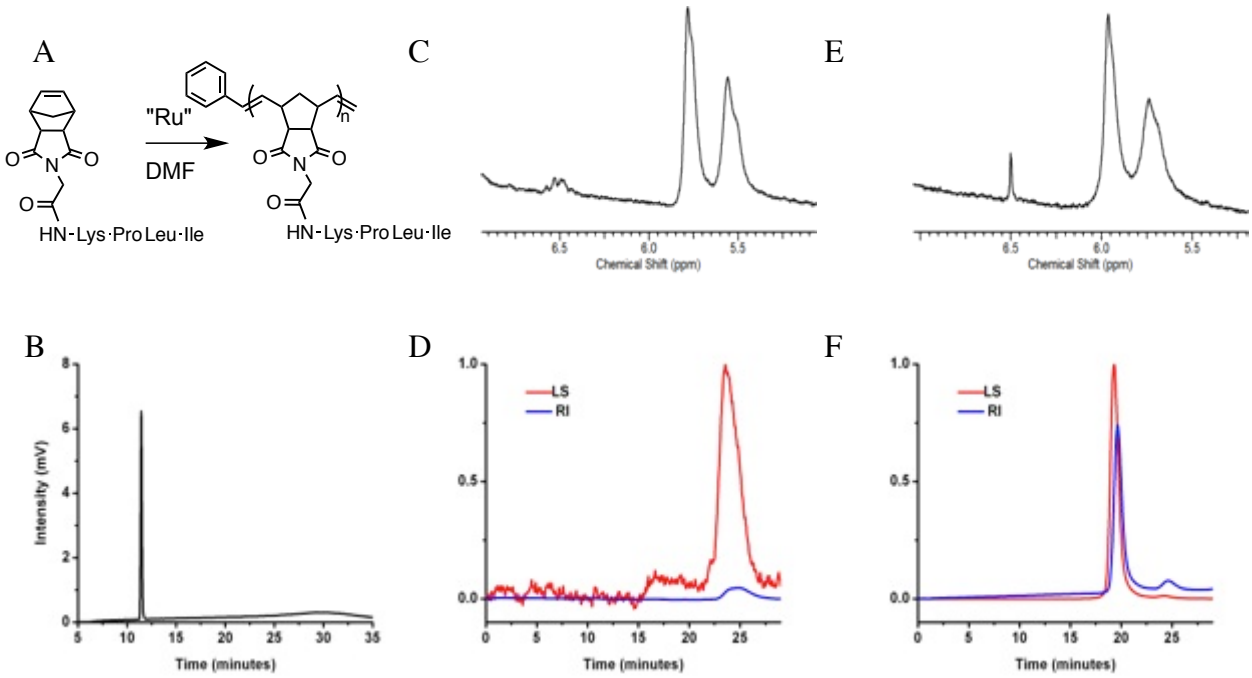


Fig. S6. Polymerization and analysis of $\mathbf{6}_{15}$ and $\mathbf{6}_{62}$

(A) Monomer and polymer structure: n = 15 or 62 (see Table 2, main text).
(B) RP-HPLC trace of **6** in 30-60% buffer B, retention time 11 minutes.
ESI-MS: Mass calc 671.4; Mass obs 672.86
(C) ^{1}H NMR of **6** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{6}_{15}$. SEC-MALS: M_n= 9,490 g/mol, PDI=1.185
(E) ^{1}H NMR of **6** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{6}_{62}$. SEC-MALS: 41,930 g/mol, PDI= 1.023

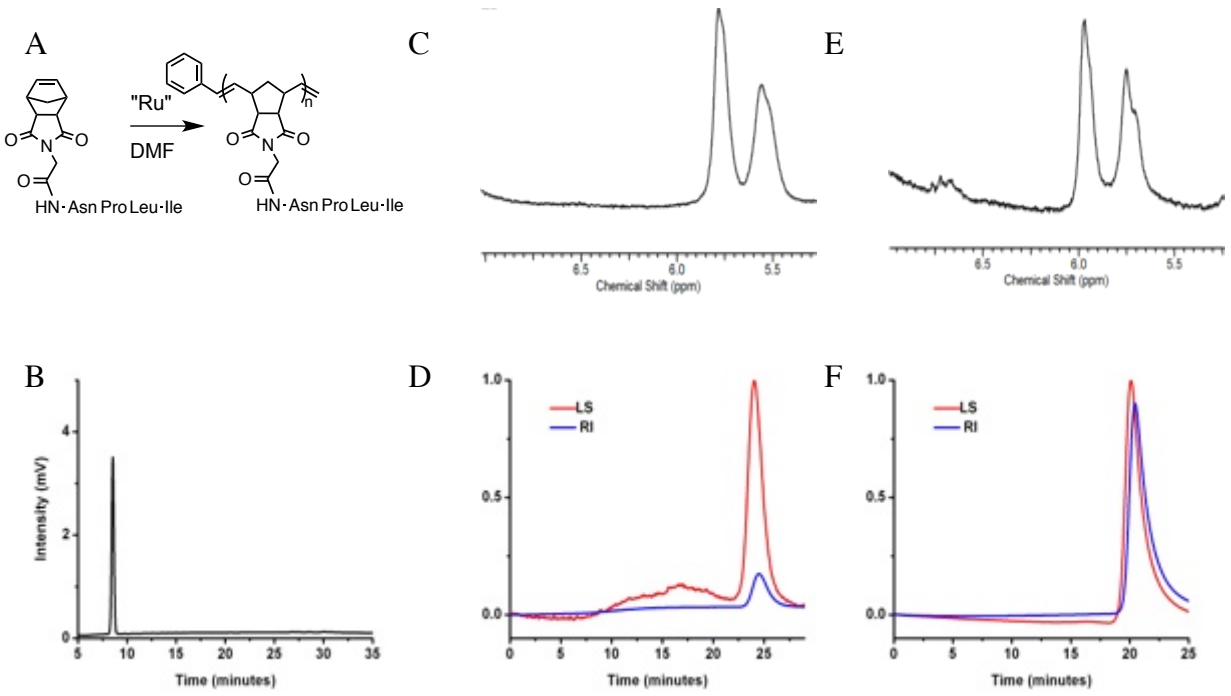


Fig. S7. Polymerization and analysis of $\mathbf{7}_{19}$ and $\mathbf{7}_{179}$

(A) Monomer and polymer structure: n = 19 and 179
(B) RP-HPLC trace of **7** in 25-43% buffer B, retention time 9 minutes.
ESI-MS: Mass calc 657.34; Mass obs 658.75
(C) ^{1}H NMR of **7** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{7}_{19}$. SEC-MALS: M_n=12,680 g/mol, PDI= 1.049
(E) ^{1}H NMR of **7** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{7}_{179}$. SEC-MALS: M_n= 117,780 g/mol, PDI= 1.017

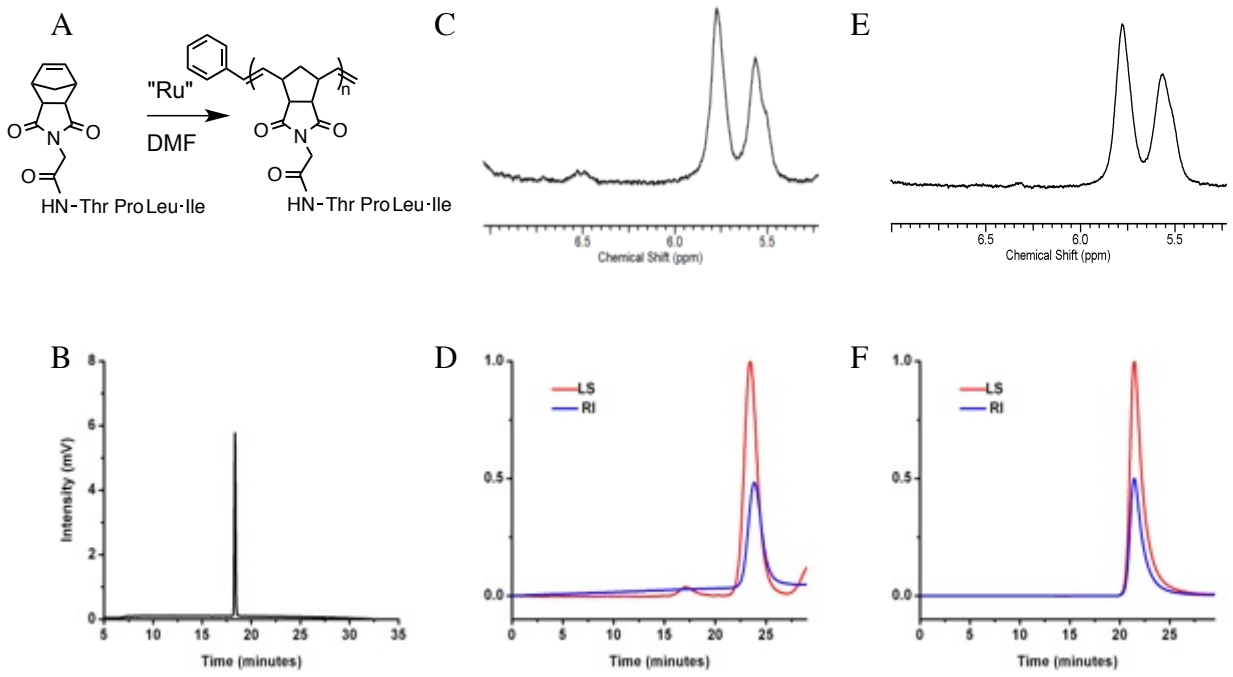


Fig. S8. Polymerization and analysis of $\mathbf{8}_{20}$ and $\mathbf{8}_{159}$

(A) Monomer and polymer structure: n = 20 or 159 (see Table 2, main text)
(B) RP-HPLC trace of **8** in 25-50% buffer B, retention time 18 minutes.
ESI-MS: Mass calc 644.35 ; Mass obs 645.94
(C) ^{1}H NMR of **8** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{8}_{20}$. SEC-MALS: M_n = 12,880 g/mol, PDI = 1.032
(E) ^{1}H NMR of **8** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{8}_{159}$. SEC-MALS: M_n =101,100 g/mol, PDI = 1.038

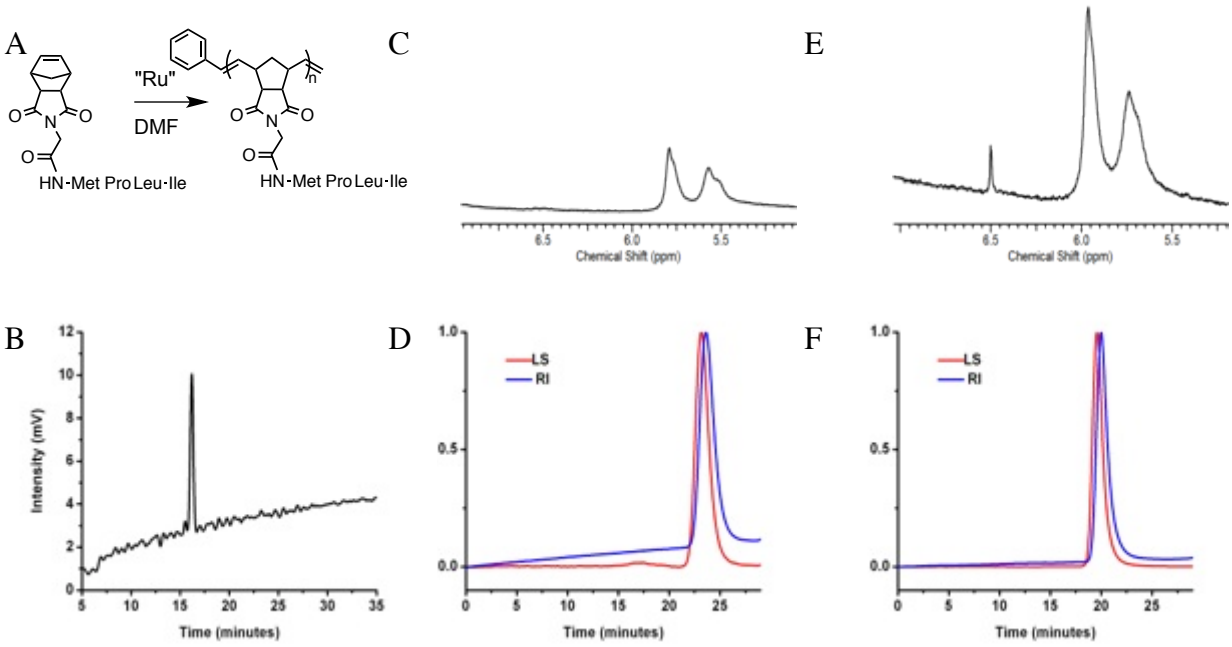


Fig. S9. Polymerization and analysis of $\mathbf{9}_{15}$ and $\mathbf{9}_{102}$

(A) Monomer and polymer structure: n = 15 or 102
(B) RP-HPLC trace of **9** in 35-45% buffer B, retention time 16 minutes.
ESI-MS: Mass calc 674.35; Mass obs 675.44
(C) ^{1}H NMR of **9** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{9}_{15}$. SEC-MALS: M_n= 10,460 g/mol, PDI= 1.036
(E) ^{1}H NMR of **9** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{9}_{102}$. SEC-MALS: 68,850 g/mol, PDI= 1.014

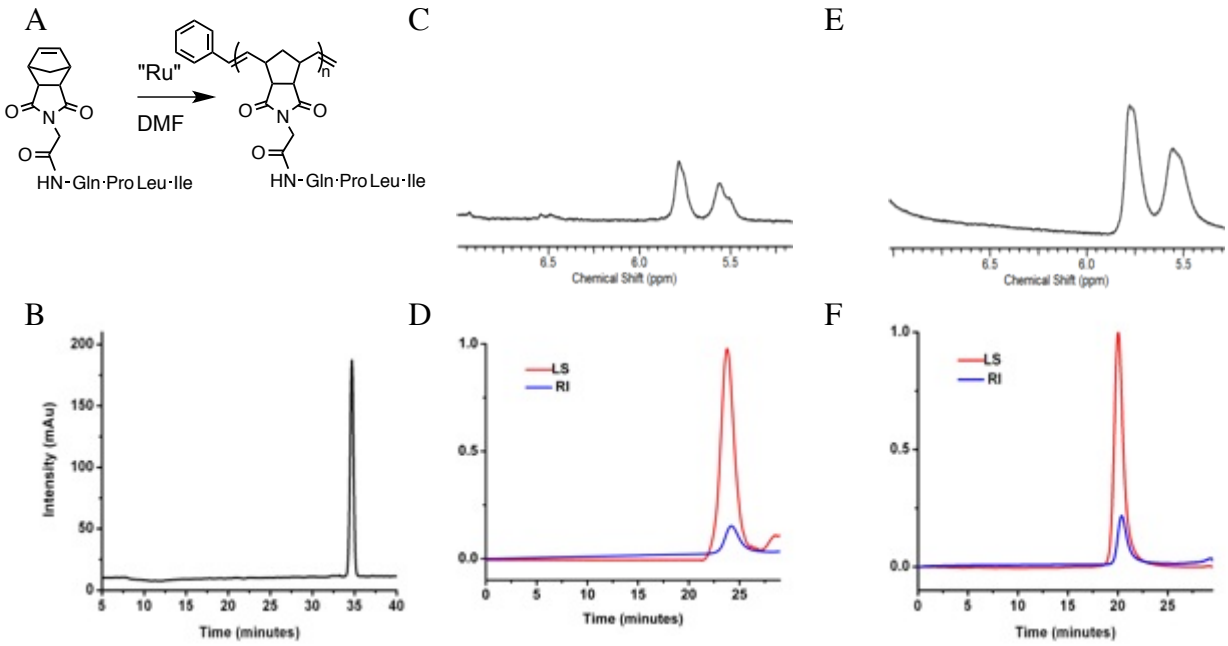


Fig. S10. Polymerization and analysis of $\mathbf{10}_{22}$ and $\mathbf{10}_{165}$

(A) Monomer and polymer structure: n = 22 or 165
(B) RP-HPLC trace of **10** in buffer 50-70%B, retention time 35 minutes.
ESI-MS: Mass calc 671.33; Mass obs 672.56
(C) ^{1}H NMR of **10** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{10}_{22}$. SEC-MALS: M_n = 15,230 g/mol, PDI = 1.053
(E) ^{1}H NMR of **10** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{10}_{165}$. SEC-MALS: M_n = 111,200 g/mol, PDI = 1.033

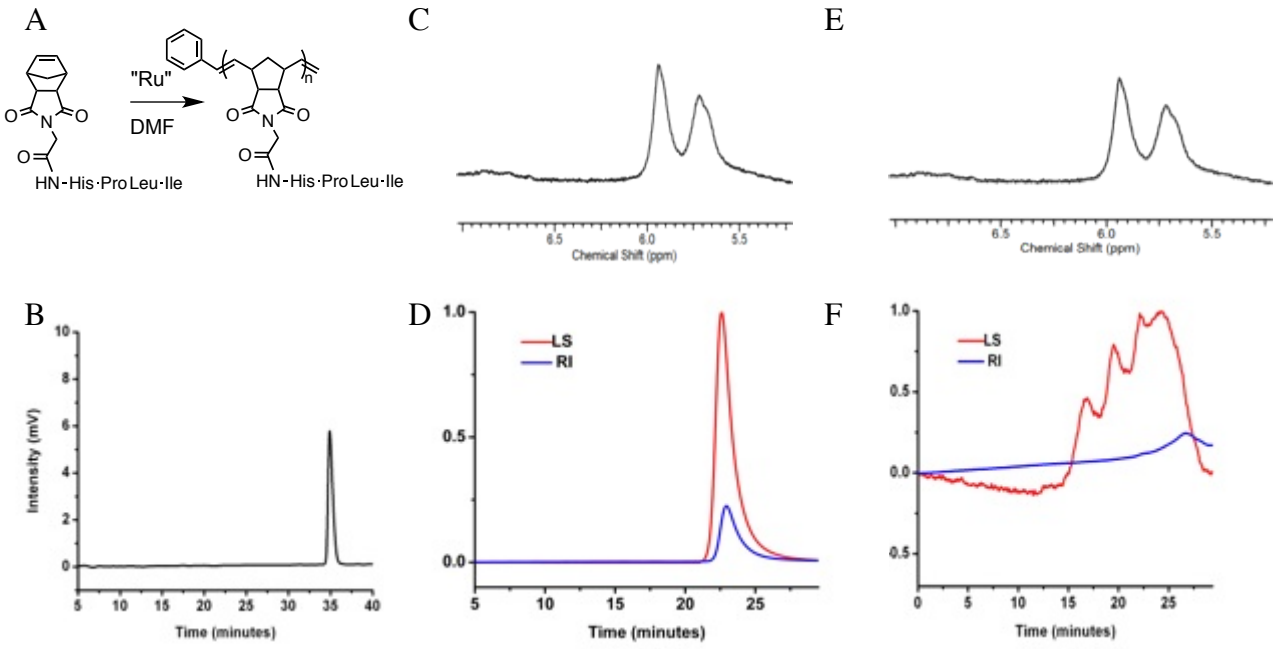


Fig. S11. Polymerization and analysis of $\mathbf{11}_{21}$ and $\mathbf{11}_{182}$

(A) Monomer and polymer structure: n = 21 or 182
(B) RP-HPLC trace of **11** in 25-50% buffer B, retention time 35 minutes.
ESI-MS: Mass calc 682.81; Mass obs 683.38
(C) ^{1}H NMR of **11** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{11}_{21}$. SEC-MALS: M_n= 14,340 g/mol, PDI= 1.102
(E) ^{1}H NMR of **11** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{11}_{182}$. SEC-MALS: M_n=124,300 g/mol, PDI= 1.201

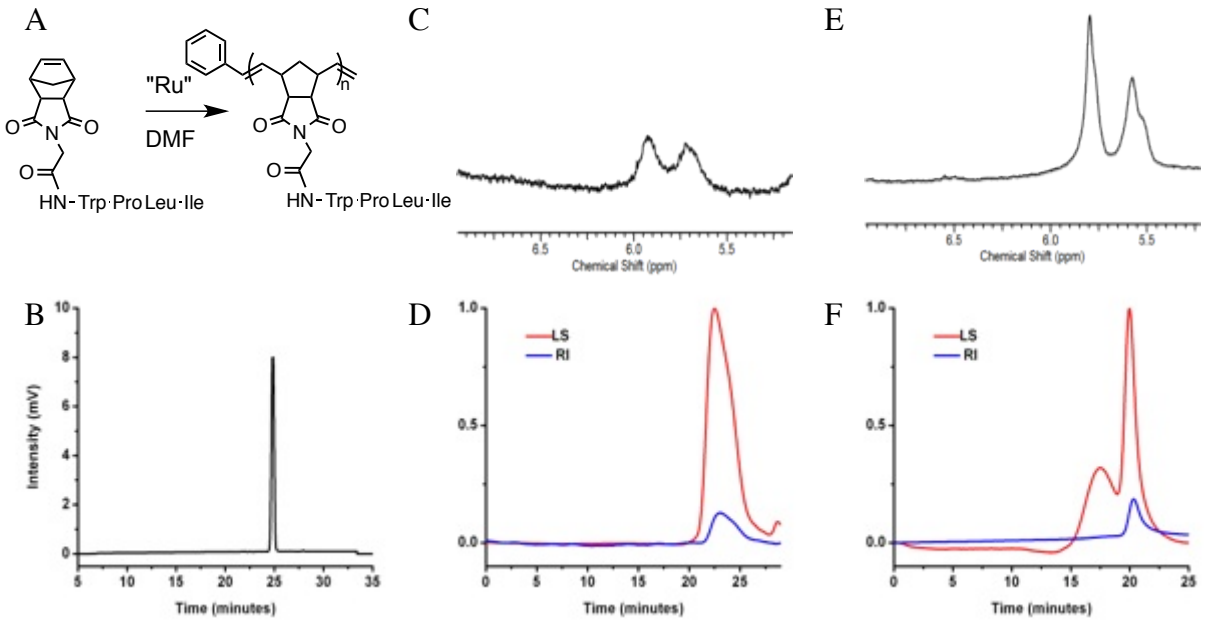


Fig. S12. Polymerization and analysis of $\mathbf{12}_{16}$ and $\mathbf{12}_{189}$

(A) Monomer and polymer structure: n = 16 or 189
(B) RP-HPLC trace of **12** in buffer 40-60% B, retention time 25 minutes.
ESI-MS: Mass calc 729.86 ; Mass obs 730.38
(C) ^{1}H NMR of **12** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{12}_{16}$. SEC-MALS: M_n = 11,670g/mol, PDI = 1.128
(E) ^{1}H NMR of **12** following monomer polymerization: M:I = 20:1
(F) SEC-MALS data of polymer $\mathbf{12}_{189}$. SEC-MALS: M_n =137,900 g/mol, PDI = 1.102

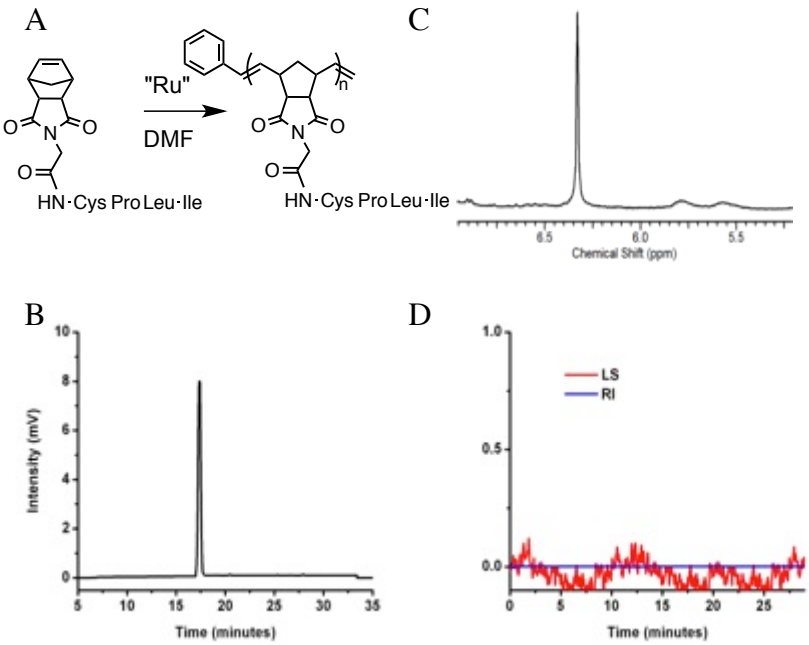


Fig. S13. Polymerization and analysis for $\mathbf{13}_3$

(A) Monomer and polymer structure: n = 3
(B) RP-HPLC trace of **13** in 30-50% buffer B, retention time 16 minutes.
ESI-MS: Mass calc 646.31; Mass obs 647.79
(C) ^{1}H NMR of **13** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{13}_3$. SEC-MALS: no Data, incomplete polymerization

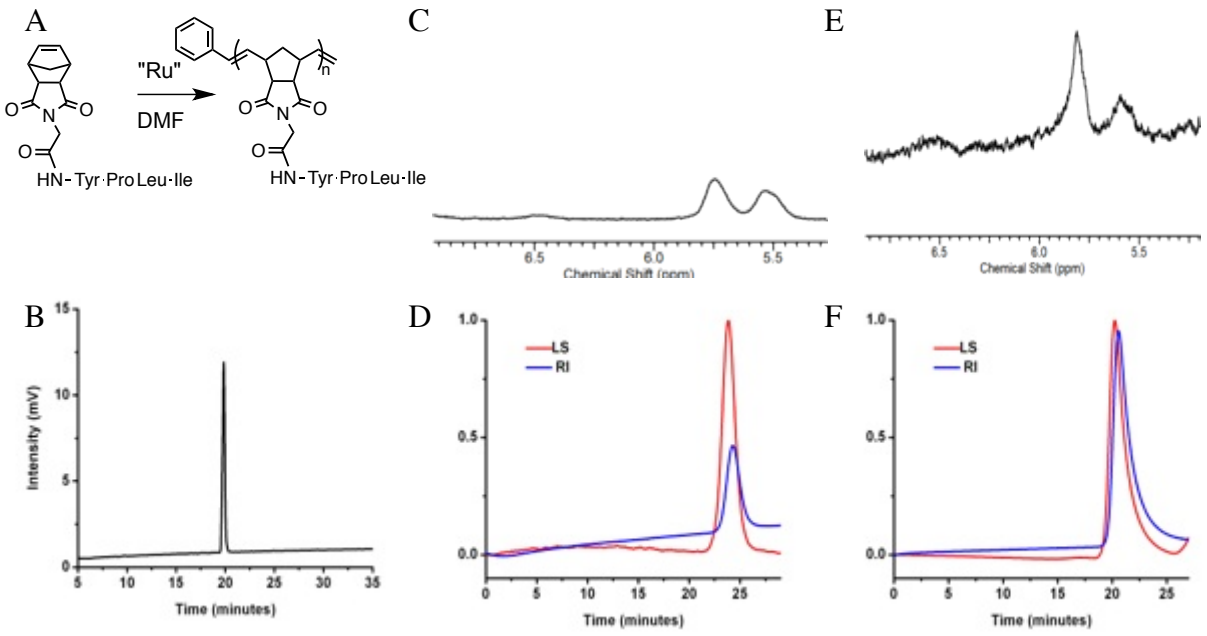


Fig. S14. Polymerization and analysis of $\mathbf{14}_{20}$ and $\mathbf{14}_{188}$

(A) Monomer and polymer structure: n = 20 and 188
(B) RP-HPLC trace of **14** in 30-60% buffer B, retention time 20 minutes.
ESI-MS: Mass calc 706.54; Mass obs 707.77
(C) ^{1}H NMR of **14** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{14}_{20}$. SEC-MALS: M_n = 14,630 g/mol, PDI = 1.096
(E) ^{1}H NMR of **14** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{14}_{188}$. SEC-MALS: M_n = 132,900 g/mol, PDI= 1.020

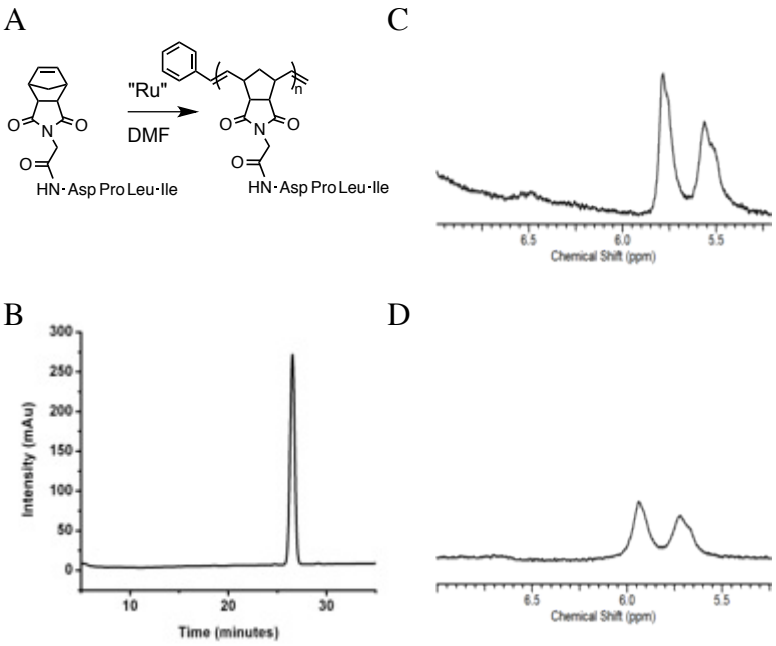


Fig. S15. Polymerization and analysis of **15**

(A) Monomer and polymer structures
(B) RP-HPLC trace of **15** in 25-45% buffer B, retention time 28 minutes.
ESI-MS: Mass calc; 658.33 Mass obs 657.89
(C) ^{1}H NMR of **15** following monomer polymerization: M:I = 20:1
(D) ^{1}H NMR of **15** following monomer polymerization: M:I = 200:1

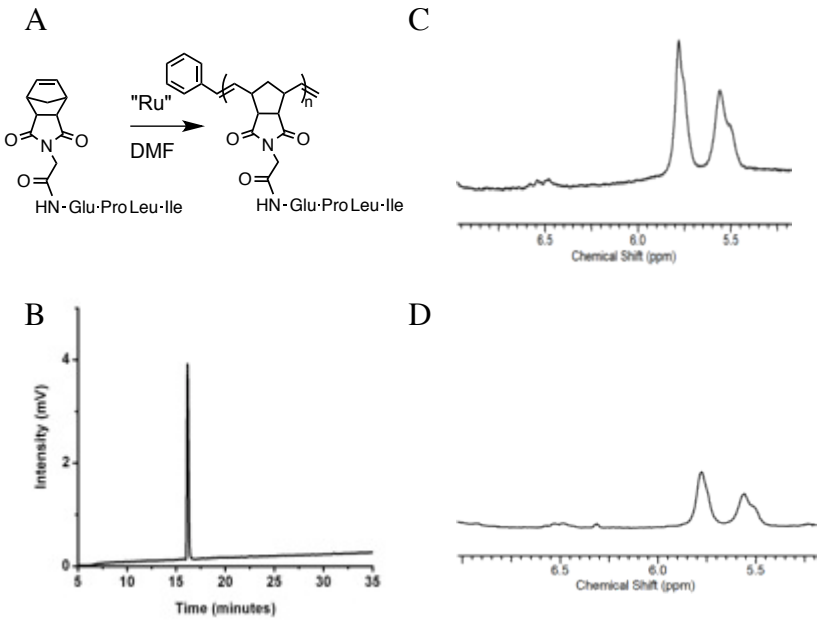


Fig. S16. Polymerization and analysis of **16**

(A) Monomer and polymer structure
(B) RP-HPLC trace of **16** in 25-80% buffer B, retention time 16 minutes. ESI-MS: Mass calc 672.35; Mass obs 671.67
(C) ^{1}H NMR of **16** following monomer polymerization: M:I = 20:1
(D) ^{1}H NMR of **16** following monomer polymerization: M:I = 200:1.

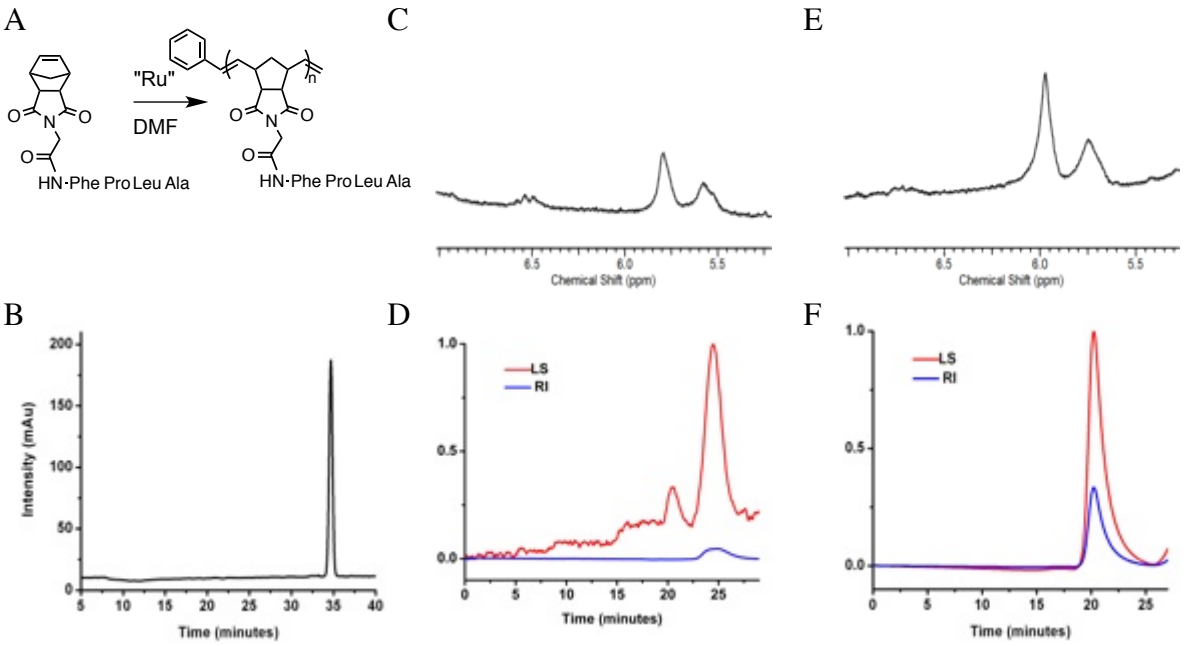


Fig. S17. Polymerization and analysis of $\mathbf{17}_{19}$ and $\mathbf{17}_{175}$

(A) Monomer and polymer structure: n = 19 or 175 (see Table 2, main text).
(B) RP-HPLC trace of **17** in 30-60% buffer B, retention time 35 minutes.
ESI-MS: Mass calc 648.33; Mass obs 649.27
(C) ^{1}H NMR of **17** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{17}_{19}$. SEC-MALS: M_n = 12,110 g/mol, PDI = 1.129
(E) ^{1}H NMR of **17** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{17}_{175}$. SEC-MALS: M_n = 113,700 g/mol, PDI = 1.034

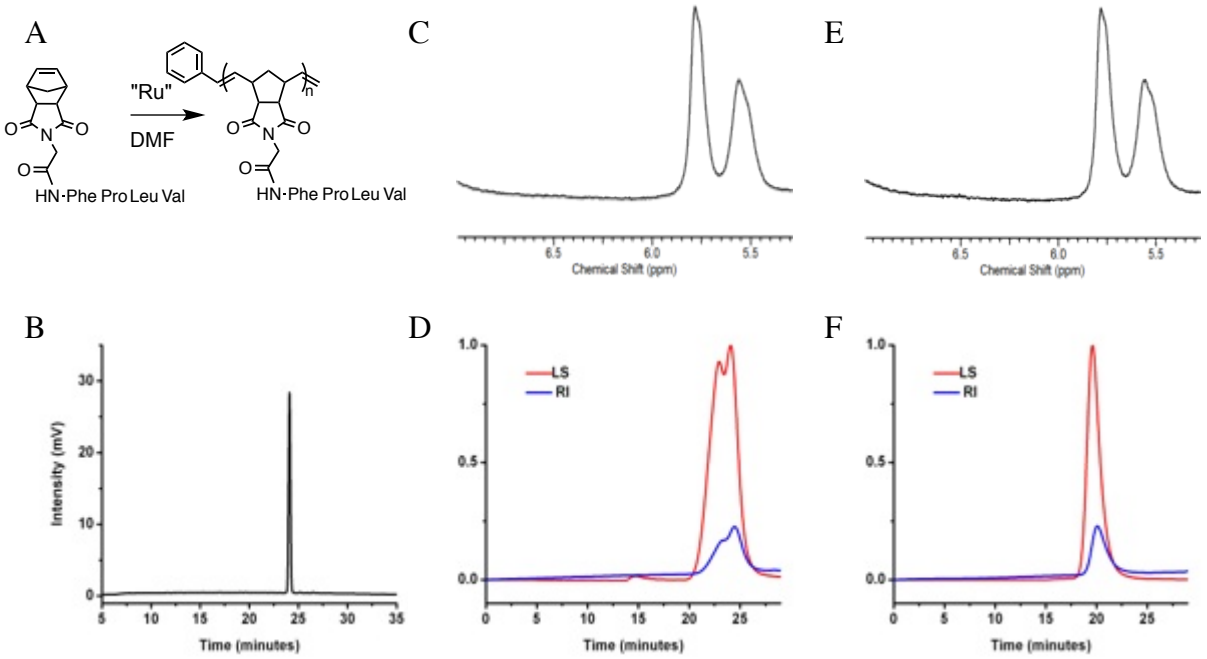


Fig. S18. Polymerization and analysis of $\mathbf{18}_{18}$ and $\mathbf{18}_{193}$

(A) Monomer and polymer structure: n = 18 or 193 (see Table 2, main text)
(B) RP-HPLC trace of **18** in 25-60% buffer B, retention time 24 minutes.
ESI-MS: Mass calc 677.35; Mass obs 678.4
(C) ^{1}H NMR of **18** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{18}_{18}$. SEC-MALS: M_n = 12,050 g/mol, PDI = 1.089
(E) ^{1}H NMR of **18** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{18}_{193}$. SEC-MALS: M_n = 130,850 g/mol, PDI = 1.04

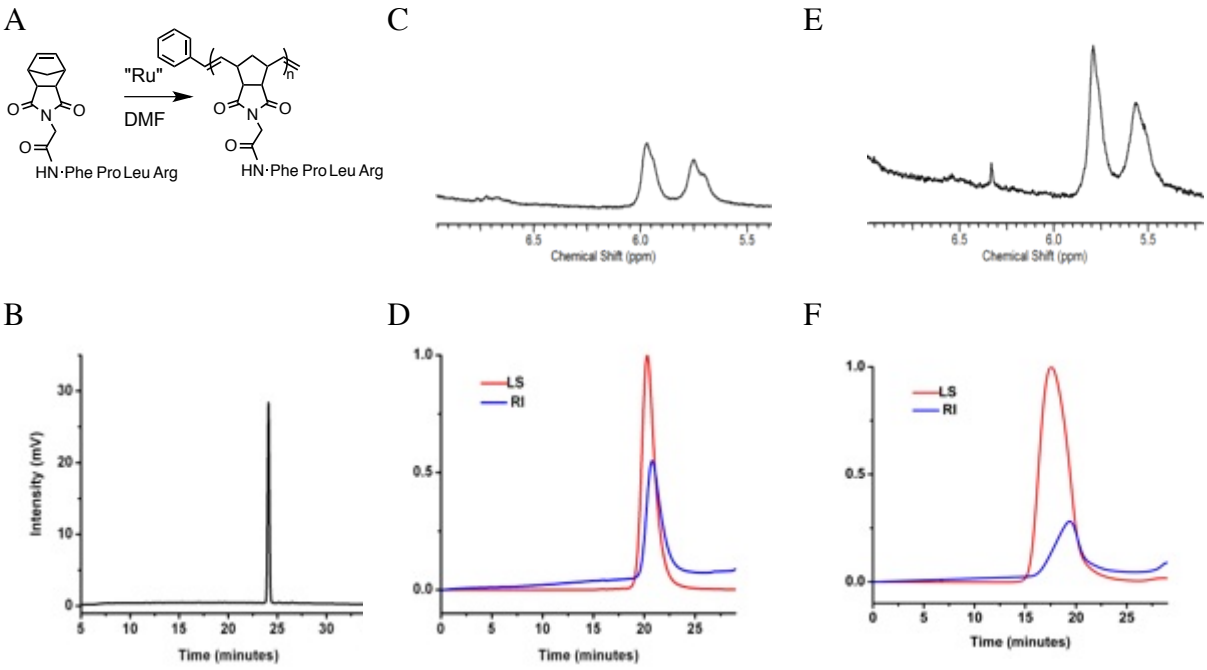


Fig. S19. Polymerization and analysis of $\mathbf{19}_{30}$ and $\mathbf{19}_{134}$

(A) Monomer and polymer structure: n = 30 or 134 (see Table 2, main text)
(B) RP-HPLC trace of **19** in 40-65% buffer B, retention time 24 minutes.
ESI-MS: Mass calc 733.39; Mass obs 734.52
(C) ^{1}H NMR of **19** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{19}_{30}$. SEC-MALS: M_n = 21,990 g/mol, PDI = 1.028
(E) ^{1}H NMR of **19** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{19}_{134}$. SEC-MALS: M_n = 98,220 g/mol, PDI = 1.356

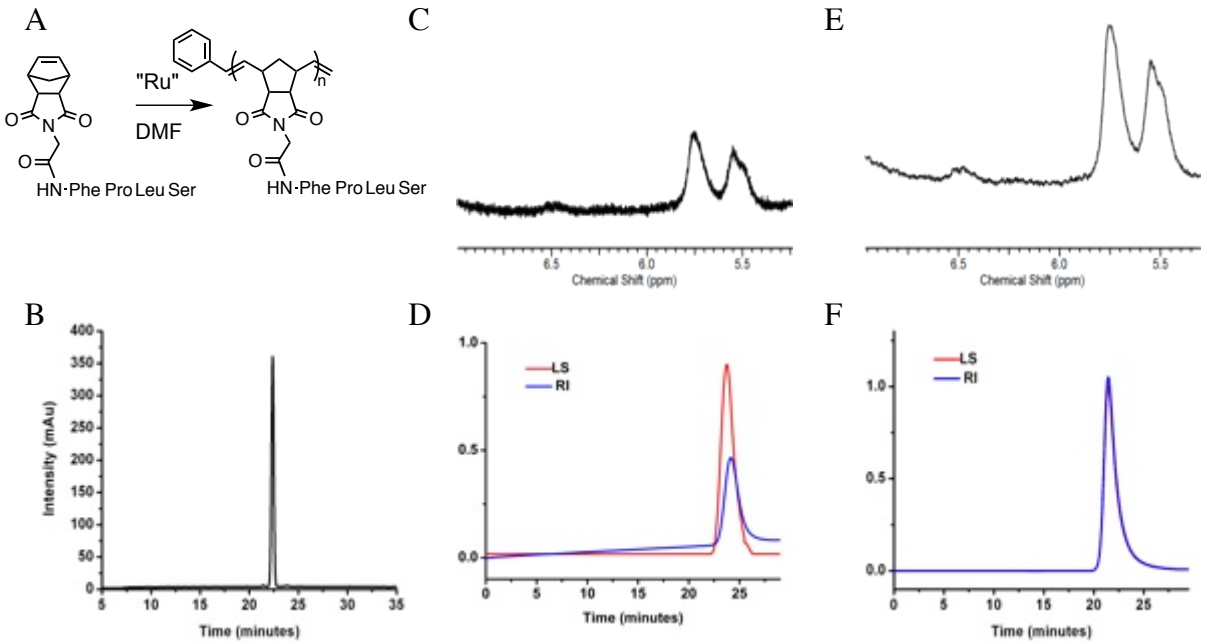


Fig. S20. Polymerization and analysis of $\mathbf{20}_{17}$ and $\mathbf{20}_{182}$

(A) Monomer and polymer structure: n = 17 or 182 (see Table 2, main text)
(B) RP-HPLC trace of **20** in 28-38% buffer B, retention time 22 minutes.
ESI-MS: Mass calc 664.32; Mass obs 665.3
(C) ^{1}H NMR of **20** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{20}_{17}$. SEC-MALS: M_n = 11,550 g/mol, PDI = 1.24
(E) ^{1}H NMR of **20** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{20}_{182}$. SEC-MALS: M_n = 120,840 g/mol, PDI = 1.003

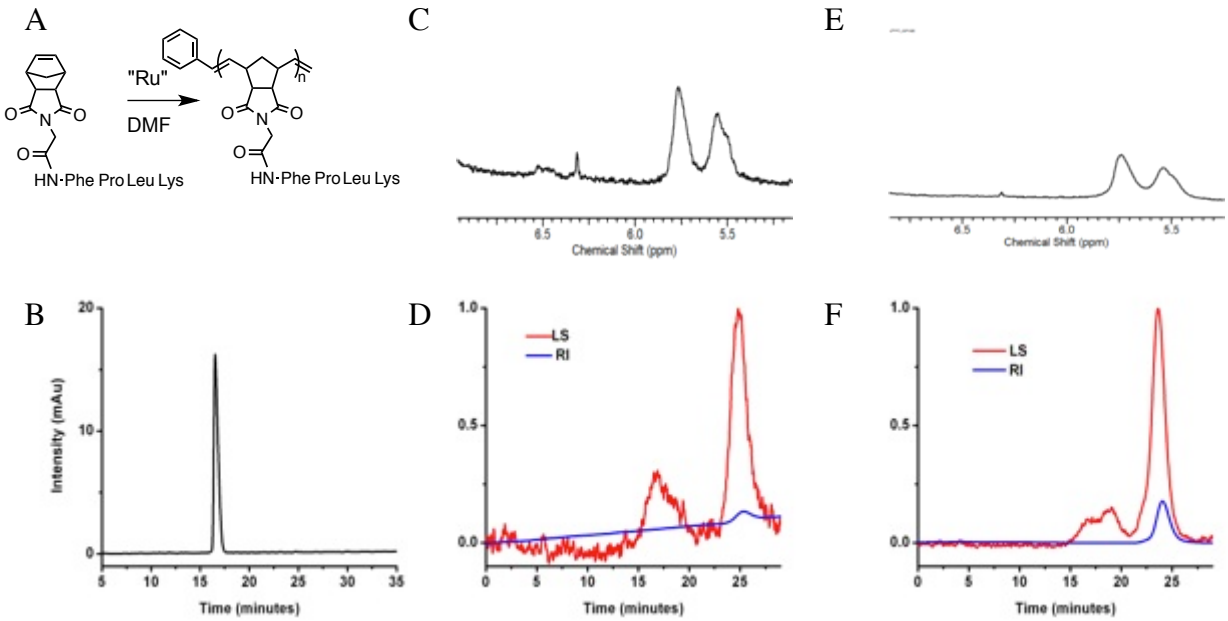


Fig. S21. Polymerization and analysis of $\mathbf{21}_{12}$ and $\mathbf{21}_{132}$

(A) Monomer and polymer structure: n = 12 or 132
(B) RP-HPLC trace of **21** in 20-60% buffer B, retention time 16 minutes.
ESI-MS: Mass calc 705.38; Mass obs 706.2
(C) ^{1}H NMR of **21** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{21}_{12}$. SEC-MALS: M_n = 8,240 g/mol, PDI = 1.045
(E) ^{1}H NMR of **21** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{21}_{132}$. SEC-MALS: M_n = 93,060 g/mol, PDI = 1.201

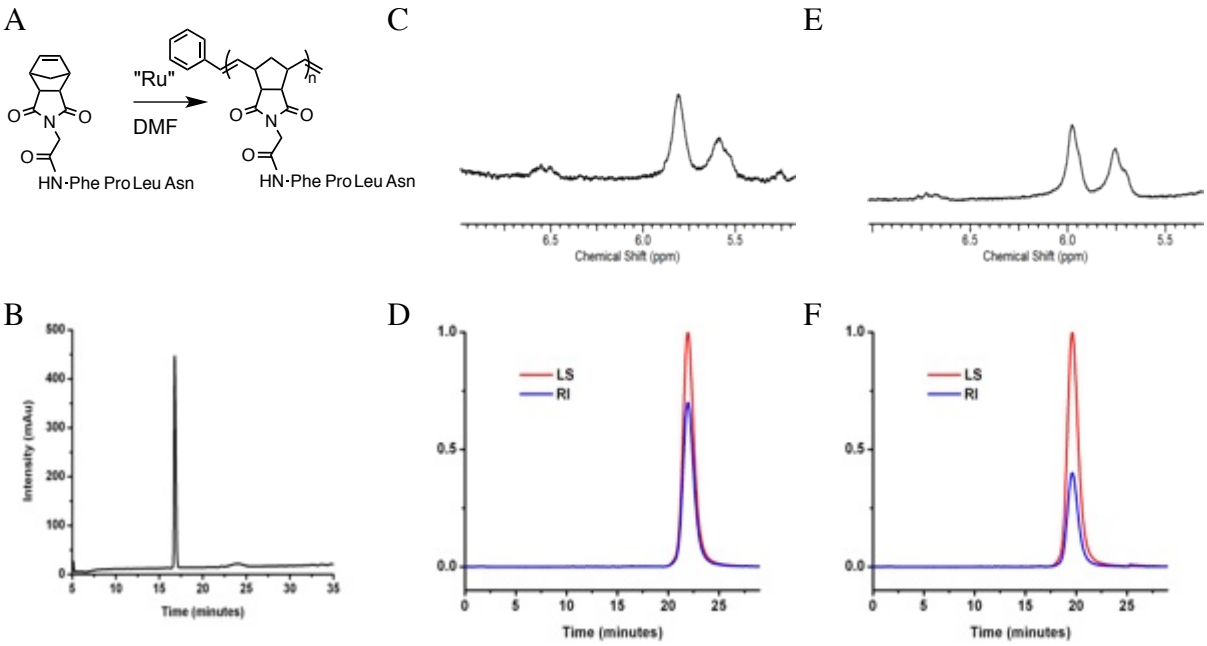


Fig. S22. Polymerization and analysis of $\mathbf{22}_{14}$ and $\mathbf{22}_{193}$

(A) Monomer and polymer structure: n = 14 or 193 (see Table 2, main text)
(B) RP-HPLC trace of **22** in 35-50% buffer B, retention time 16 minutes.
ESI-MS: Mass calc 691.71; Mass obs 692.1
(C) ^{1}H NMR of **22** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{22}_{14}$. SEC-MALS: M_n = 9,890 g/mol, PDI = 1.043
(E) ^{1}H NMR of **22** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{22}_{193}$. SEC-MALS: M_n = 133,500 g/mol, PDI = 1.032

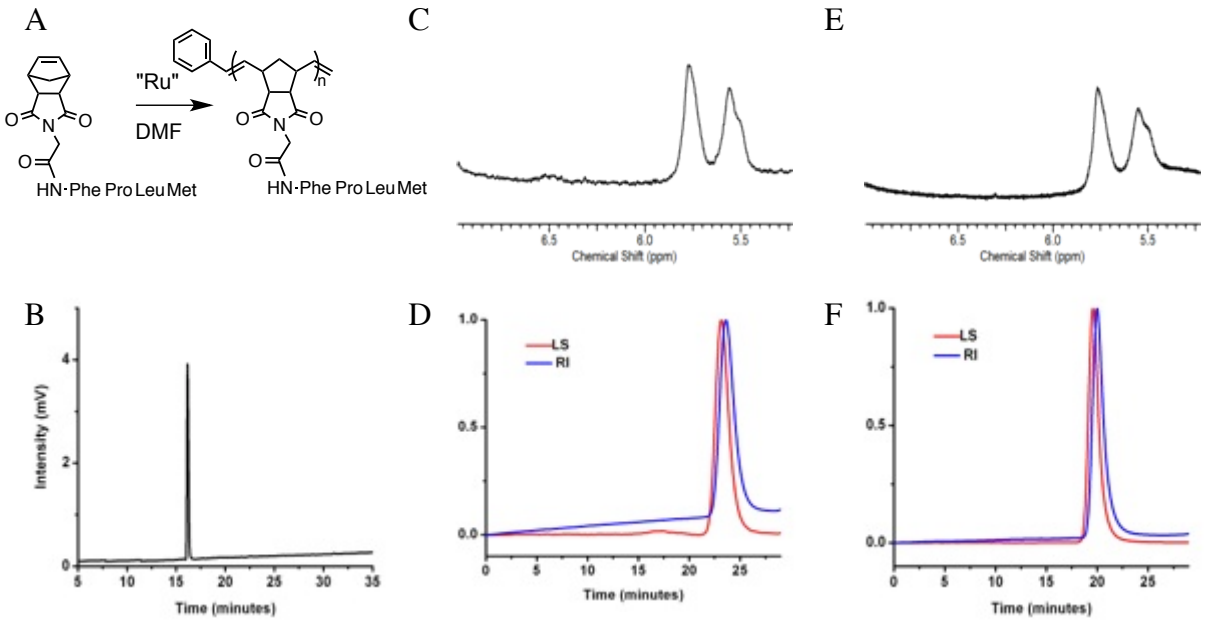


Fig. S23. Polymerization and analysis of $\mathbf{23}_{15}$ and $\mathbf{23}_{157}$

(A) Monomer and polymer structure: n = 15 or 157 (see Table 2, main text)
(B) RP-HPLC trace of **23** in 35-50% buffer B, retention time 16 minutes.
ESI-MS: Mass calc 708.33; Mass obs 709.1
(C) ^{1}H NMR of **23** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{23}_{15}$. SEC-MALS: M_n = 10,940 g/mol, PDI = 1.036
(E) ^{1}H NMR of **23** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{23}_{157}$. SEC-MALS: M_n = 111,310 g/mol, PDI = 1.018

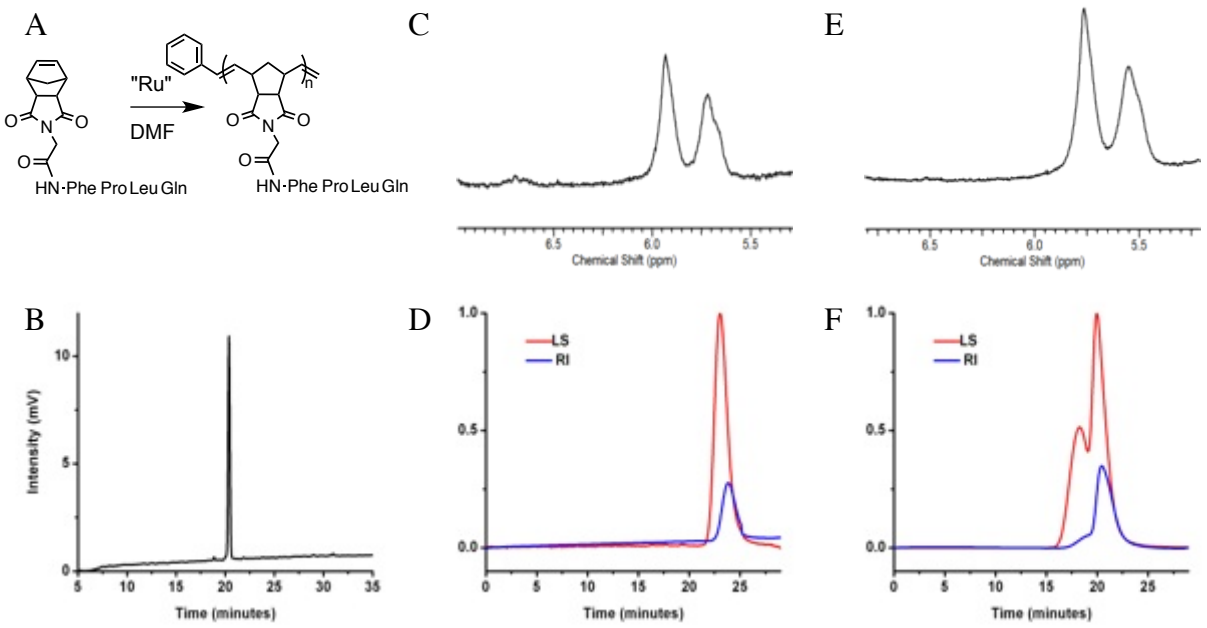


Fig. S24. Polymerization and analysis of $\mathbf{24}_{15}$ and $\mathbf{24}_{163}$

(A) Monomer and polymer structure: n = 15 or 163 (see Table 2, main text)
(B) RP-HPLC trace of **24** in 30-40% buffer B, retention time 20 minutes.
ESI-MS: Mass calc 705.80; Mass obs 706.3
(C) ^{1}H NMR of **24** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{24}_{15}$. SEC-MALS: M_n = 10,890 g/mol, PDI = 1.037
(E) ^{1}H NMR of **24** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{24}_{163}$. SEC-MALS: M_n = 115,400 g/mol, PDI = 1.109

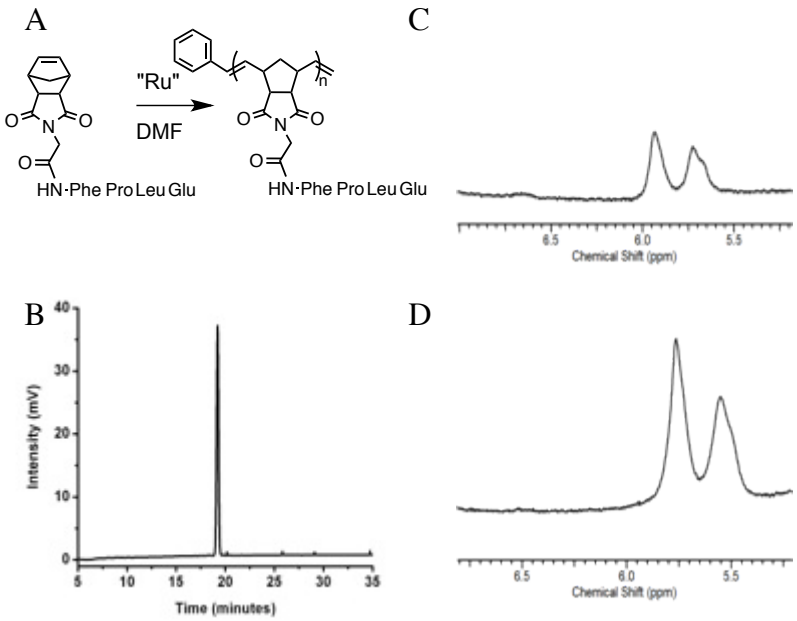


Fig. S25. Polymerization and analysis of **25**

(A) Monomer and polymer structure
(B) RP-HPLC trace of **25** in 30-55% buffer B, retention time 19 minutes.
ESI-MS: Mass calc 706.79; Mass obs 707.2
(C) ^{1}H NMR of **25** following monomer polymerization: M:I = 20:1
(D) ^{1}H NMR of **25** following monomer polymerization: M:I = 200:1.

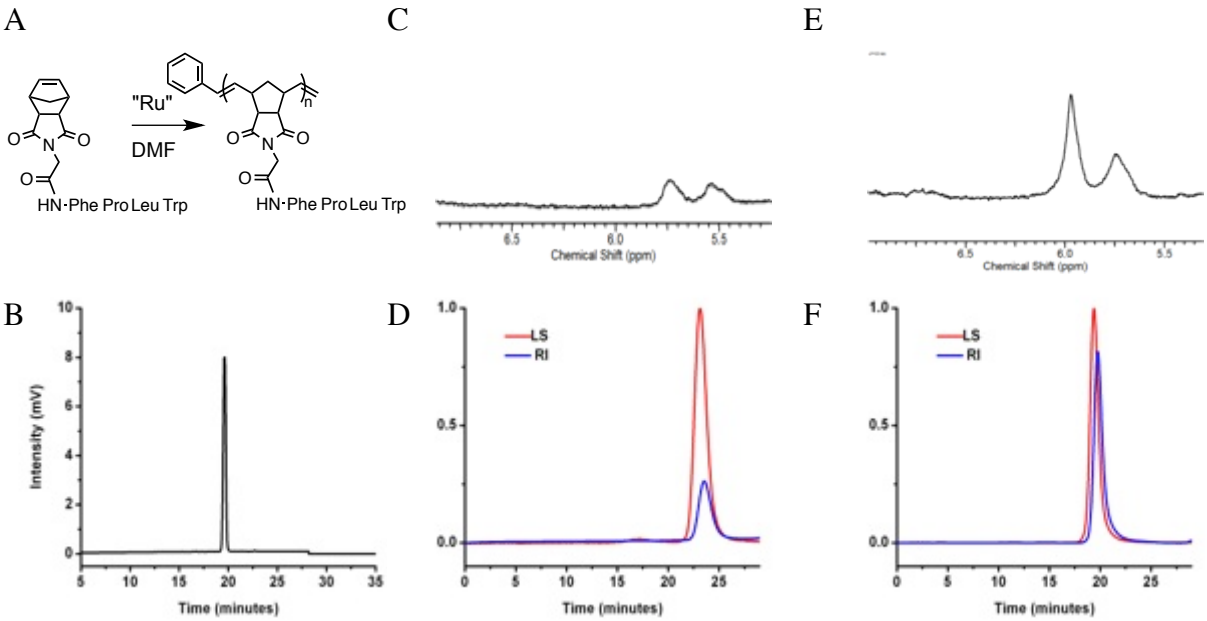


Fig. S26. Polymerization and analysis of $\mathbf{26}_{25}$ and $\mathbf{26}_{216}$

(A) Monomer and polymer structure: n = 25 or 216 (see Table 2, main text)
(B) RP-HPLC trace of **26** in 60-70% buffer B, retention time 20 minutes.
ESI-MS: Mass calc=763.88; Mass obs= 764.2
(C) ^{1}H NMR of **26** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{26}_{25}$. SEC-MALS: M_n = 19,070 g/mol, PDI = 1.022
(E) ^{1}H NMR of **26** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{26}_{216}$. SEC-MALS: M_n = 164,800 g/mol, PDI = 1.015

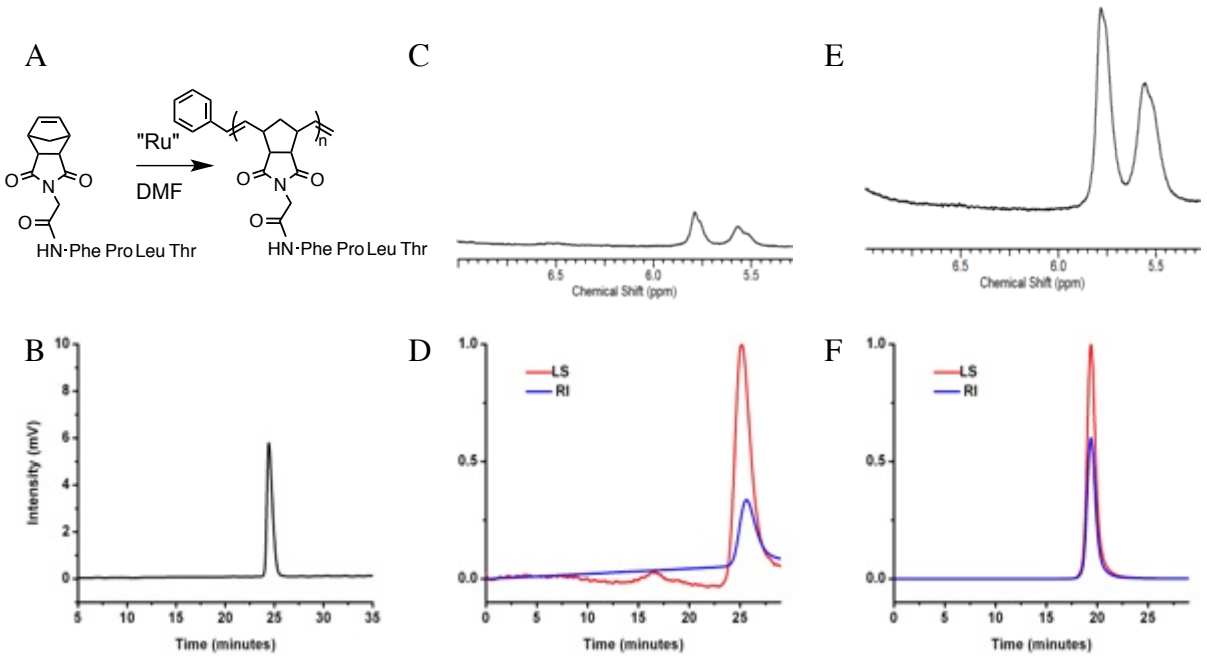


Fig. S27. Polymerization and analysis of $\mathbf{27}_{14}$ and $\mathbf{27}_{187}$

(A) Monomer and polymer structure: n = 14 or 187 (see Table 2, main text)
(B) RP-HPLC trace of **27** in 35-50% buffer B, retention time 25 minutes.
ESI-MS: Mass calc 678.34; Mass obs 678.8
(C) ^{1}H NMR of **27** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of the polymer $\mathbf{27}_{14}$. SEC-MALS: M_n = 10,170 g/mol, PDI = 1.22
(E) ^{1}H NMR of **27** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{27}_{187}$. SEC-MALS: M_n =126,780 g/mol, PDI = 1.020

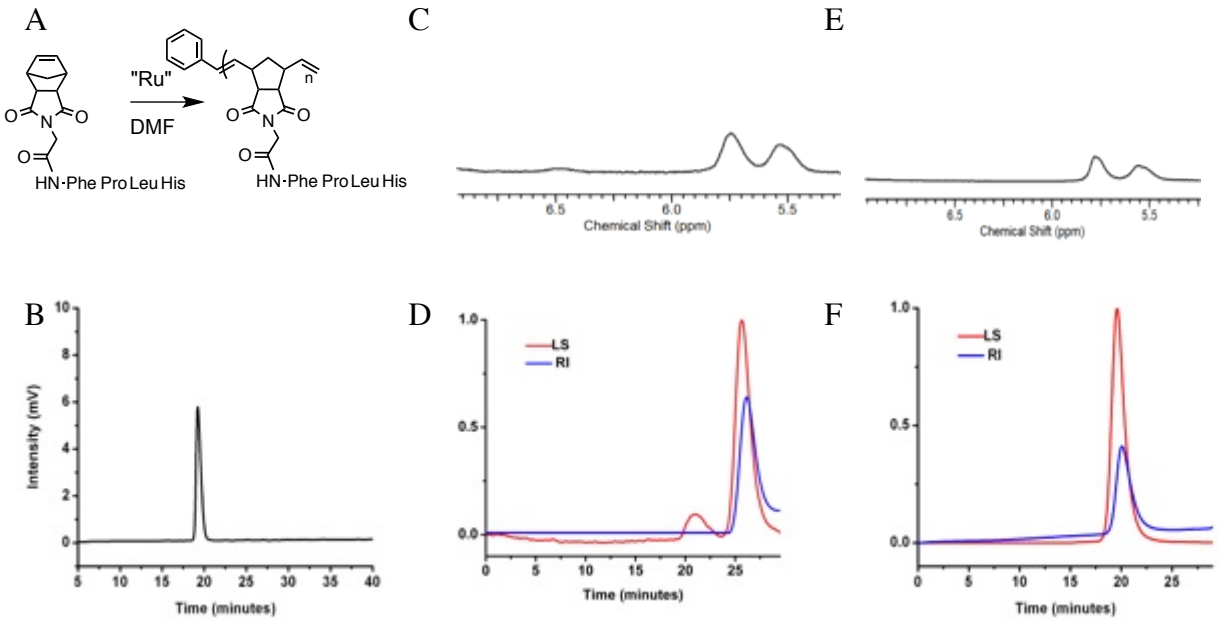


Fig. S28. Polymerization and analysis of $\mathbf{28}_{17}$ and $\mathbf{28}_{182}$

(A) Monomer and polymer structure: n = 17 or 182 (see Table 2, main text)
(B) RP-HPLC trace of **28** in 30-40% buffer B, retention time 19 minutes.
ESI-MS: Mass calc 714.35; Mass obs 714.8
(C) ^{1}H NMR of **28** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{28}_{1}$. SEC-MALS: M_n = 12,130 g/mol, PDI = 1.100
(E) ^{1}H NMR of **28** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{28}_{182}$. SEC-MALS: M_n = 137,800 g/mol, PDI = 1.026

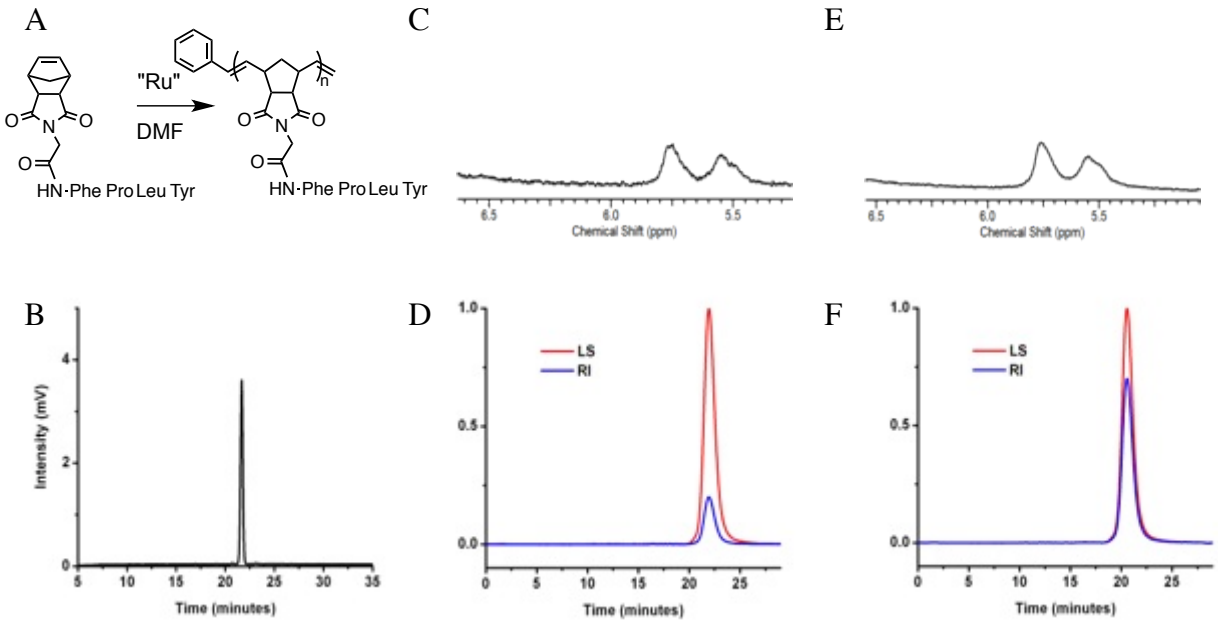


Fig. S29. Polymerization and analysis of $\mathbf{29}_{20}$ and $\mathbf{29}_{192}$

(A) Monomer and polymer structure: n = 20 or 192 (see Table 2, main text)
(B) RP-HPLC trace of **29** in 30-50% buffer B, retention time 22 minutes.
ESI-MS: Mass calc 740.35; Mass obs 741.3
(C) ^{1}H NMR of **29** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{29}_{20}$. SEC-MALS: M_n = 14,920 g/mol, PDI = 1.196
(E) ^{1}H NMR of **29** following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer $\mathbf{29}_{192}$. SEC-MALS: M_n = 143,280 g/mol, PDI = 1.019

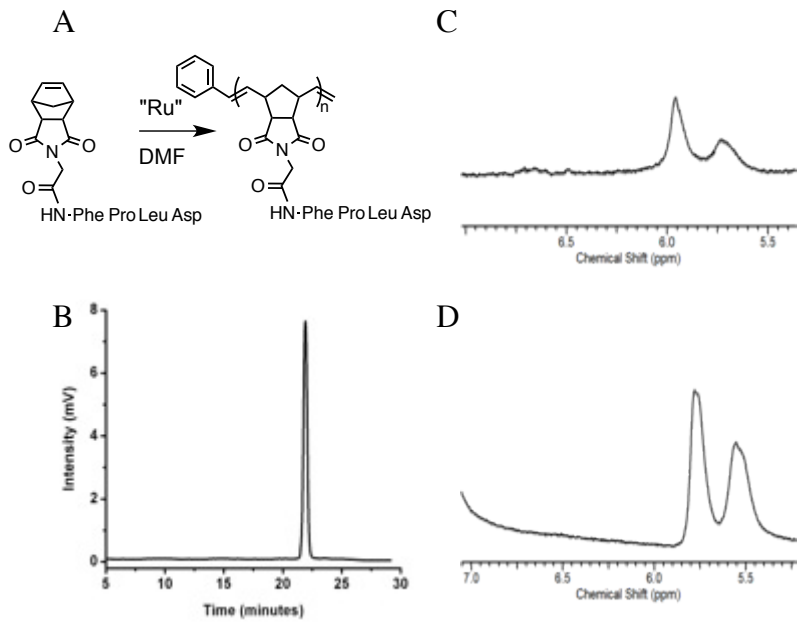


Fig. S30. Polymerization and analysis of **30**

(A) Monomer and polymer structure
(B) RP-HPLC trace of **30** in 35-45% buffer B, retention time 22 minutes. ESI-MS: Mass calc 682.32; Mass obs 692.9
(C) ^{1}H NMR of **30** following monomer polymerization: M:I = 20:1
(D) ^{1}H NMR of **30** following monomer polymerization: M:I = 200:1

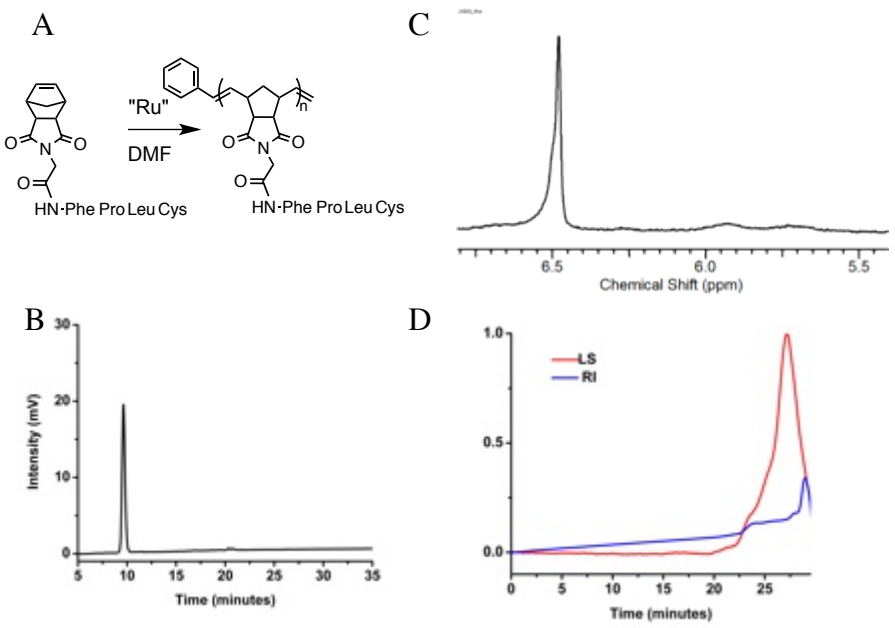


Fig. S31. Polymerization and analysis of $\mathbf{31}_6$

(A) Monomer and polymer structure: n = 6
(B) RP-HPLC trace of **31** in 40-60% buffer B, retention time 10 minutes.
ESI-MS: Mass calc 680.30; Mass obs 680.9
(C) ^{1}H NMR of **31** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{31}_6$. SEC-MALS: M_n = 3,870 g/mol, PDI = 1.456

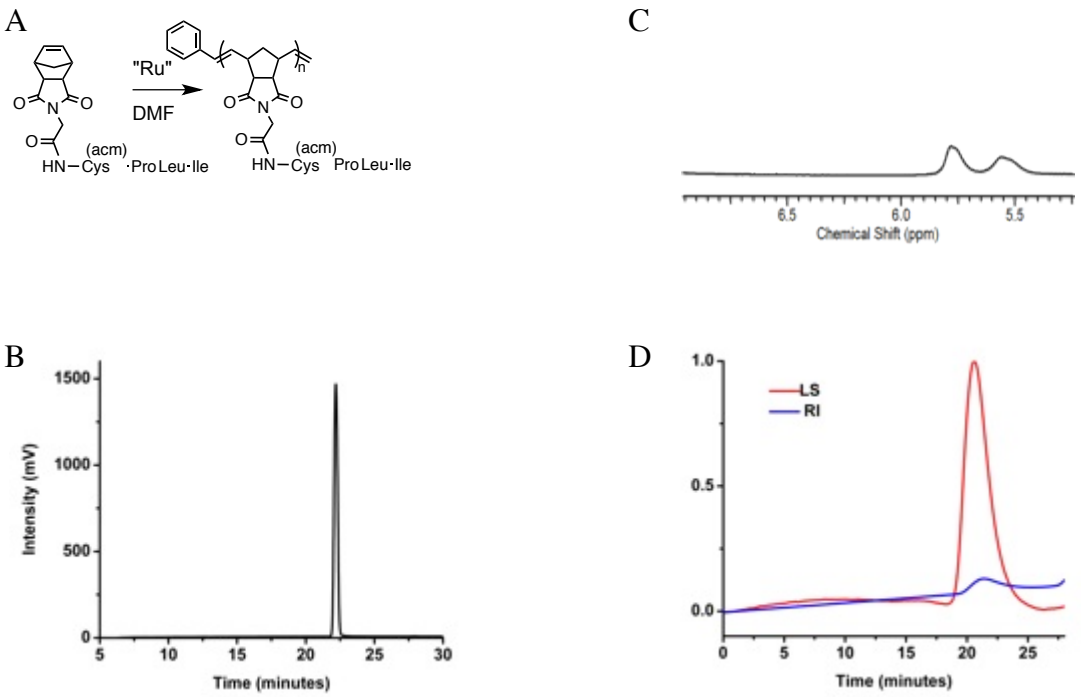
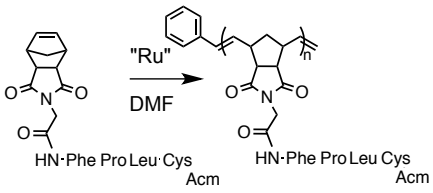


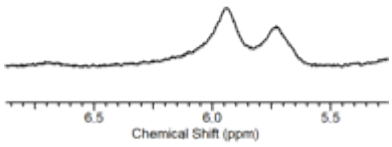
Figure S32. Polymerization and analysis of protected analogue of **13**

(A) Monomer and polymer structure: n = 12
(B) RP-HPLC trace in 35-50% buffer B, retention time 22 minutes.
ESI-MS: Mass calc 717.35 ; Mass obs 717.66
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n = 8500 g/mol, PDI = 1.408

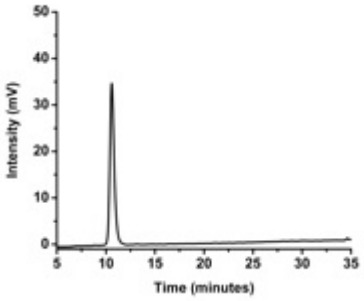
A



C



B



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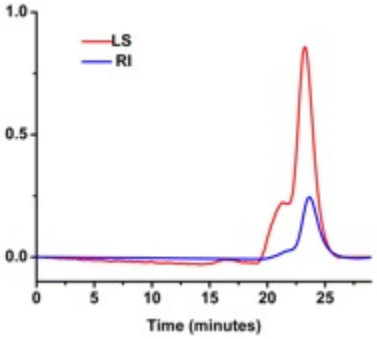

Fig. S33. Polymerization and analysis of protected analogue of **31**

(A) Monomer and polymer structure: n = 21
(B) RP-HPLC trace in 35-50% buffer B, retention time 11 minutes.
ESI-MS: Mass calc 751.34; Mass obs 751.34
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n = 16,100 g/mol, PDI = 1.100

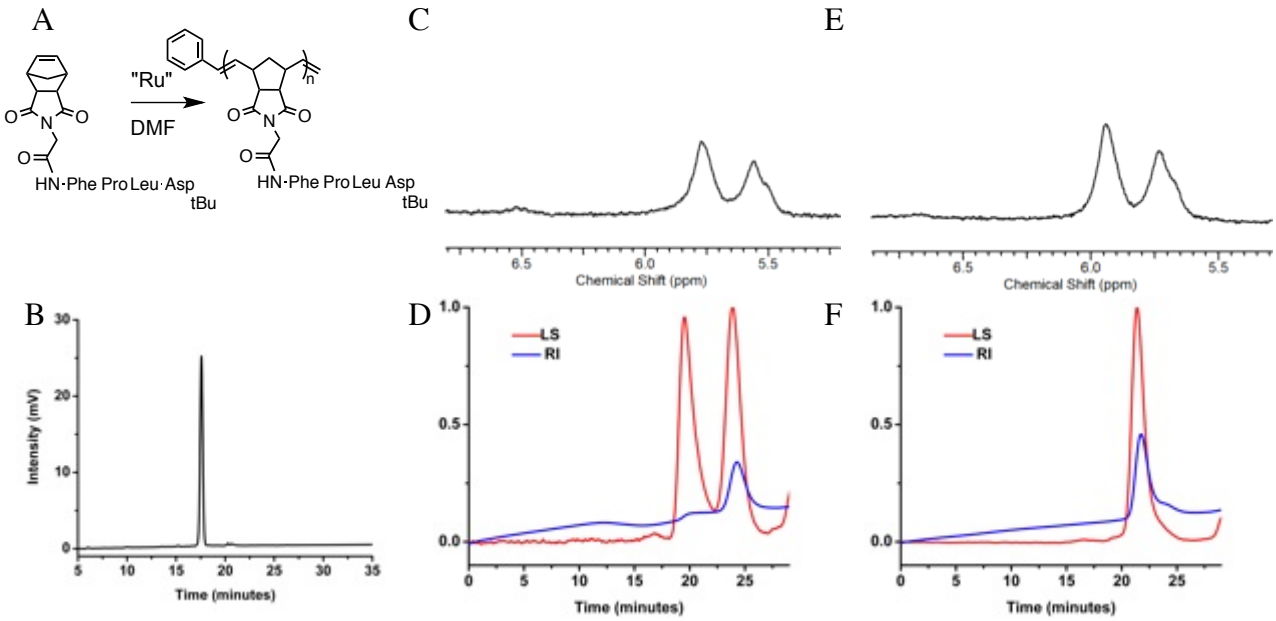

Fig. S34. Polymerization and analysis of a protected analogue of **30**

(A) Monomer and polymer structure: n = 12 or 188
(B) RP-HPLC trace in 40-60% buffer B, retention time 17 minutes.
ESI-MS: Mass calc 748.38; Mass obs 748.7
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n = 8,970 g/mol, PDI = 1.017
(E) ^{1}H NMR following monomer polymerization: M:I = 200:1
(F) SEC-MALS data of polymer SEC-MALS: M_n = 141,000 g/mol, PDI = 1.162

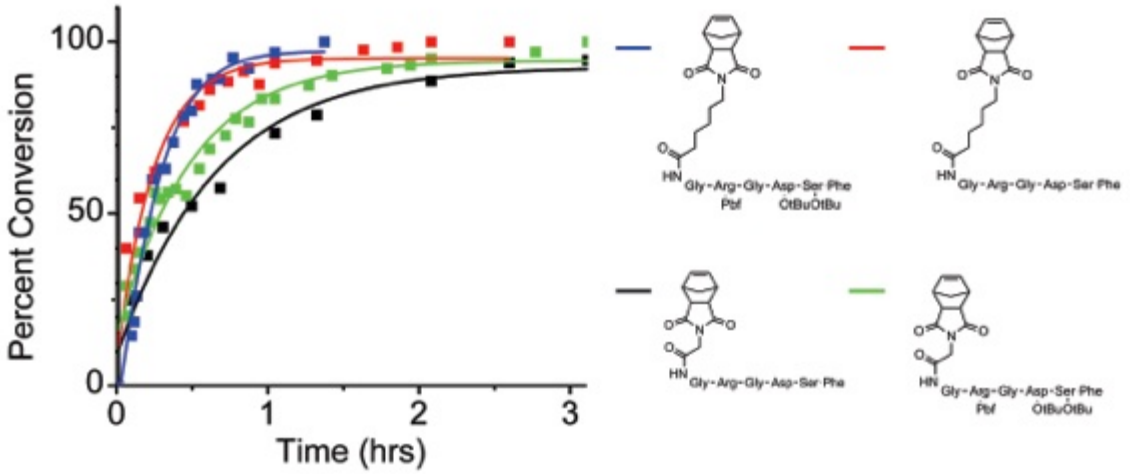

Fig. S35. Polymerization of Nor-GRGDSF analogs

(A) Percent conversion as determined by ^{1}H NMR for NorGGRGDSF, NorGGR(pbf)GD(tBu)S(tBu)F, NorAhaGRGDSF and NorAhaGR(pbf)GD(tBu)S(tBu)F.

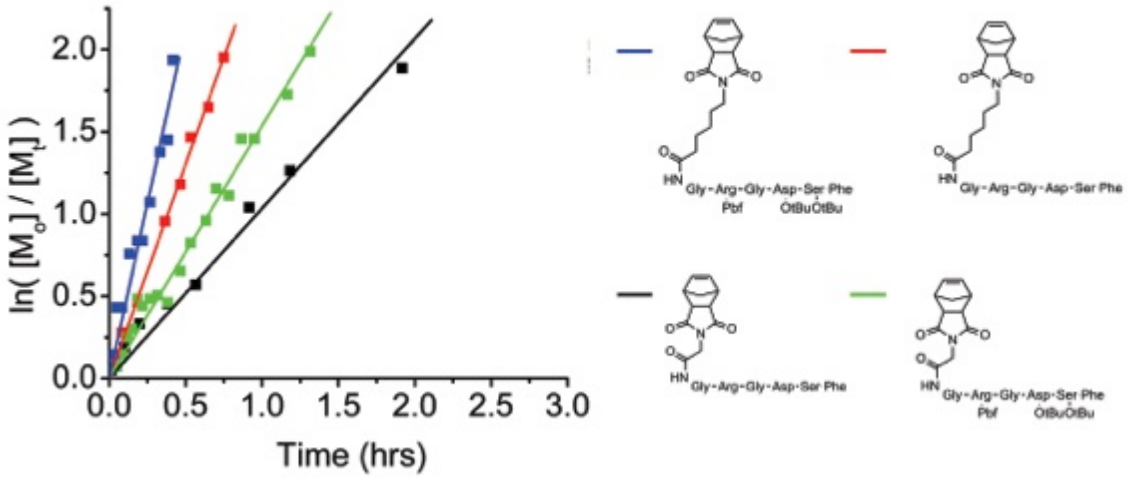

Fig. S36. Polymerization rates of NorGGRGDSF analogs

Log plots of the rate of polymerization as determined by integration of the olefin peaks by ^{1}H NMR for NorGGRGDSF, NorGGR(pbf)GD(tBu)S(tBu)F, NorAhaGRGDSF and NorAhaGR(pbf)GD(tBu)S(tBu)F. The following slopes (k_{obs}) were determined by linear least-squares fitting of the plots: 4.3 hr^{-1},2.6 hr^{-1}, 1.5 hr^{-1}, and 1.0 hr^{-1} for NorAhaGR(pbf)GD(tBu)S(tBu)F NorAhaGRGDSF, NorGGR(pbf)GD(tBu)S(tBu)F, and NorGGRGDSF respectively.

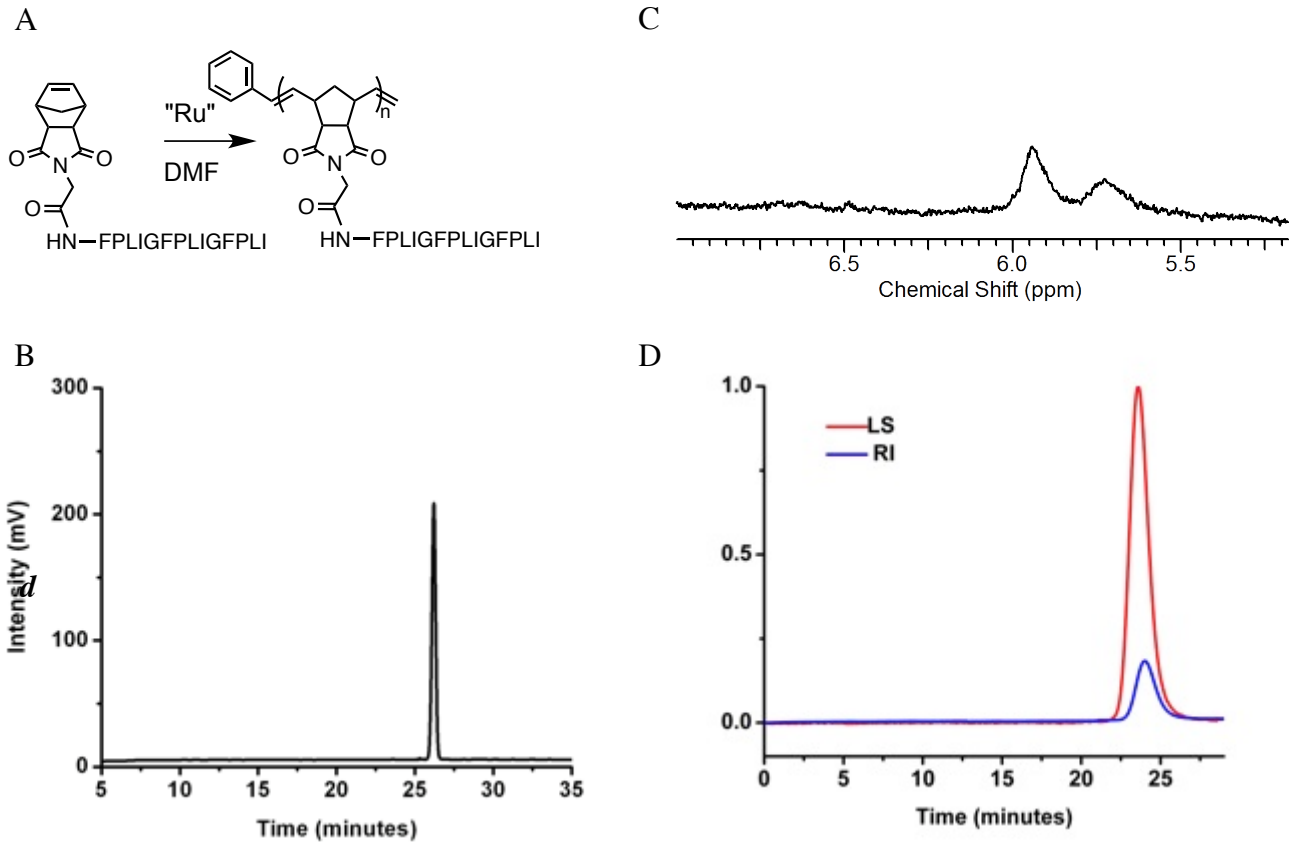

Fig. S37. Polymerization and analysis of $\mathbf{36_{18}}$

(A) Monomer and polymer structure: n = 18
(B) RP-HPLC trace of **36** in 60-75% buffer B, retention time 26 minutes.
ESI-MS: Mass calc 1077.5 ; Mass obs 1077.9
(C) ^{1}H NMR of **36** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{36_{18}}$. SEC-MALS: M_n = 21,500 g/mol, PDI = 1.037

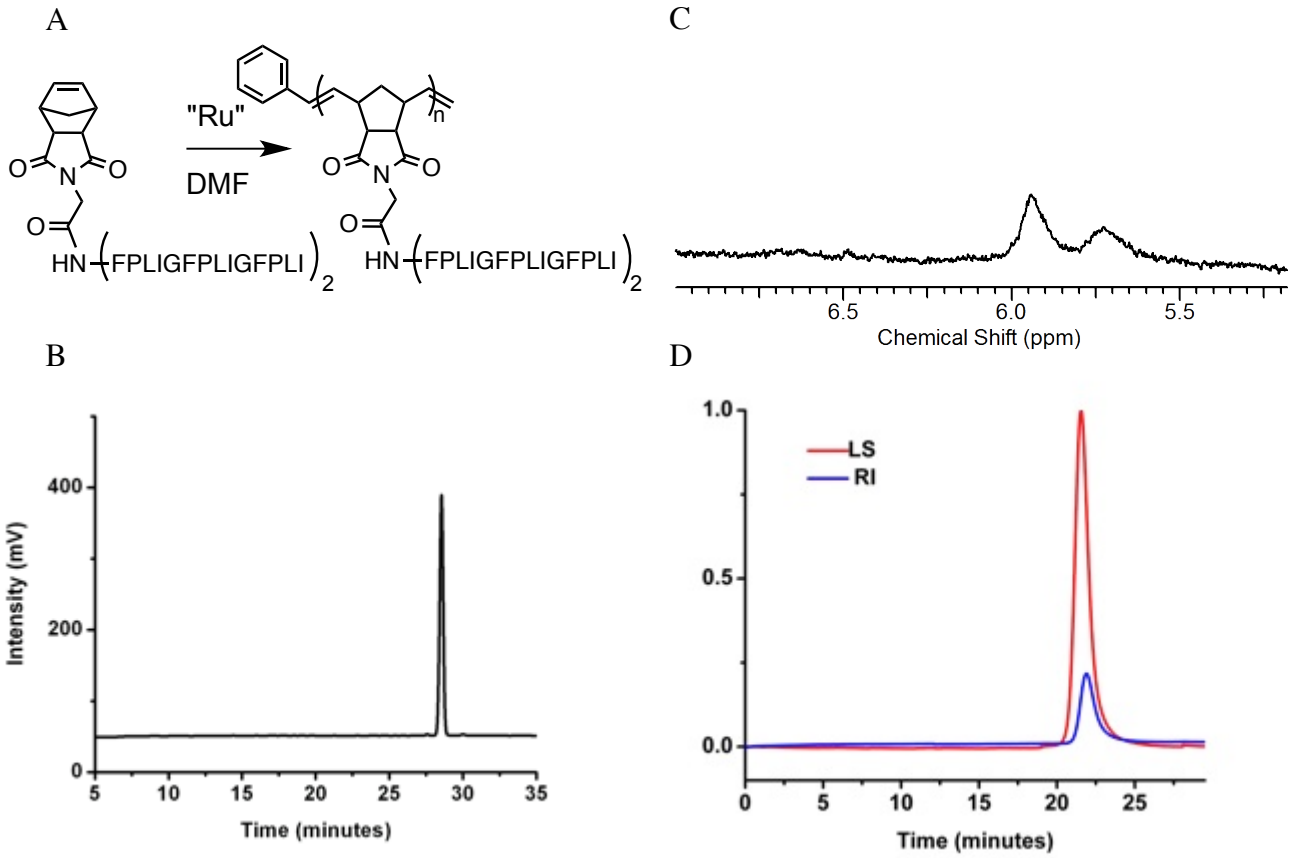

Figure 38S. Polymerization and analysis of **37**$_{18}$

(A) Monomer and polymer structure: n = 18
(B) RP-HPLC trace of **37** in 65-75% buffer B, retention time 28 minutes.
ESI-MS: Mass calc 2707.5 ; Mass obs 2707.9
(C) ^{1}H NMR of **37** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer **37**$_{18}$. SEC-MALS: M_n = 52,140 g/mol, PDI = 1.037

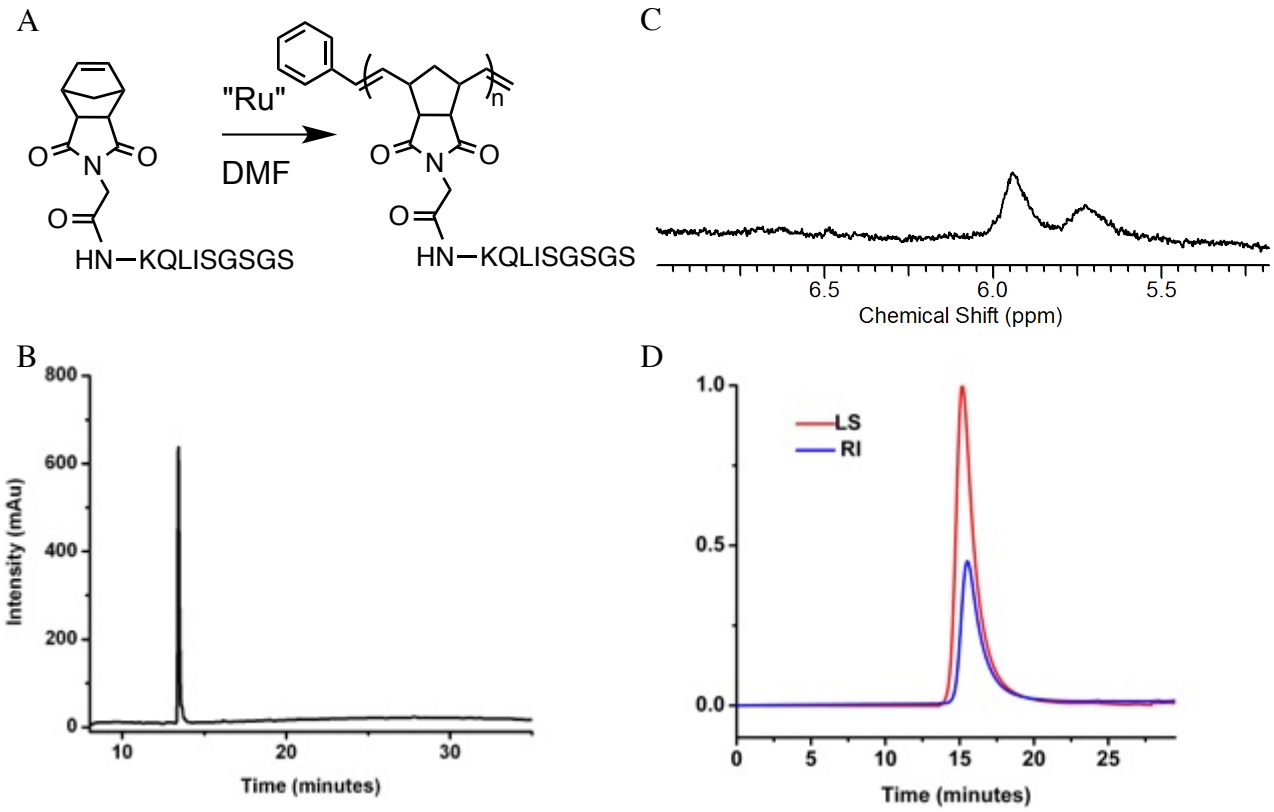

Figure S39. Polymerization and analysis of $\mathbf{38}_{21}$

(A) Monomer and polymer structure: n = 21
(B) RP-HPLC trace of **38** in 30-50% buffer B, retention time 13 minutes.
ESI-MS: Mass calc 1077.5 ; Mass obs 1077.9
(C) ^{1}H NMR of **38** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer $\mathbf{38}_{21}$. SEC-MALS: M_n = 21,500 g/mol, PDI = 1.037

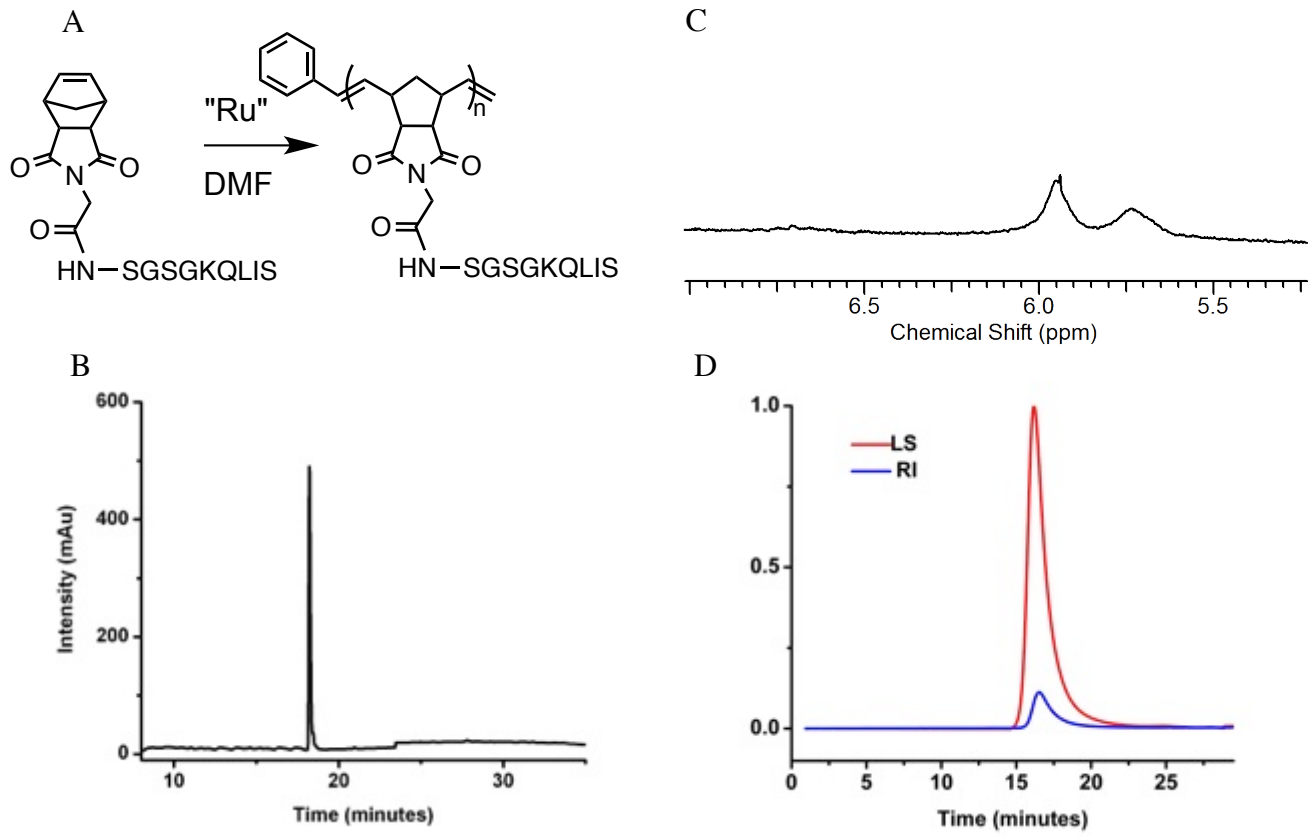

Figure S40. Polymerization and analysis of **39**$_{19}$

(A) Monomer and polymer structure: n = 19
(B) RP-HPLC trace of **39** in 30-50% buffer B, retention time 13 minutes.
ESI-MS: Mass calc 1077.5 ; Mass obs 1077.9
(C) ^{1}H NMR of **39** following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer **39**$_{19}$. SEC-MALS: M_n = 21,470 g/mol, PDI = 1.023

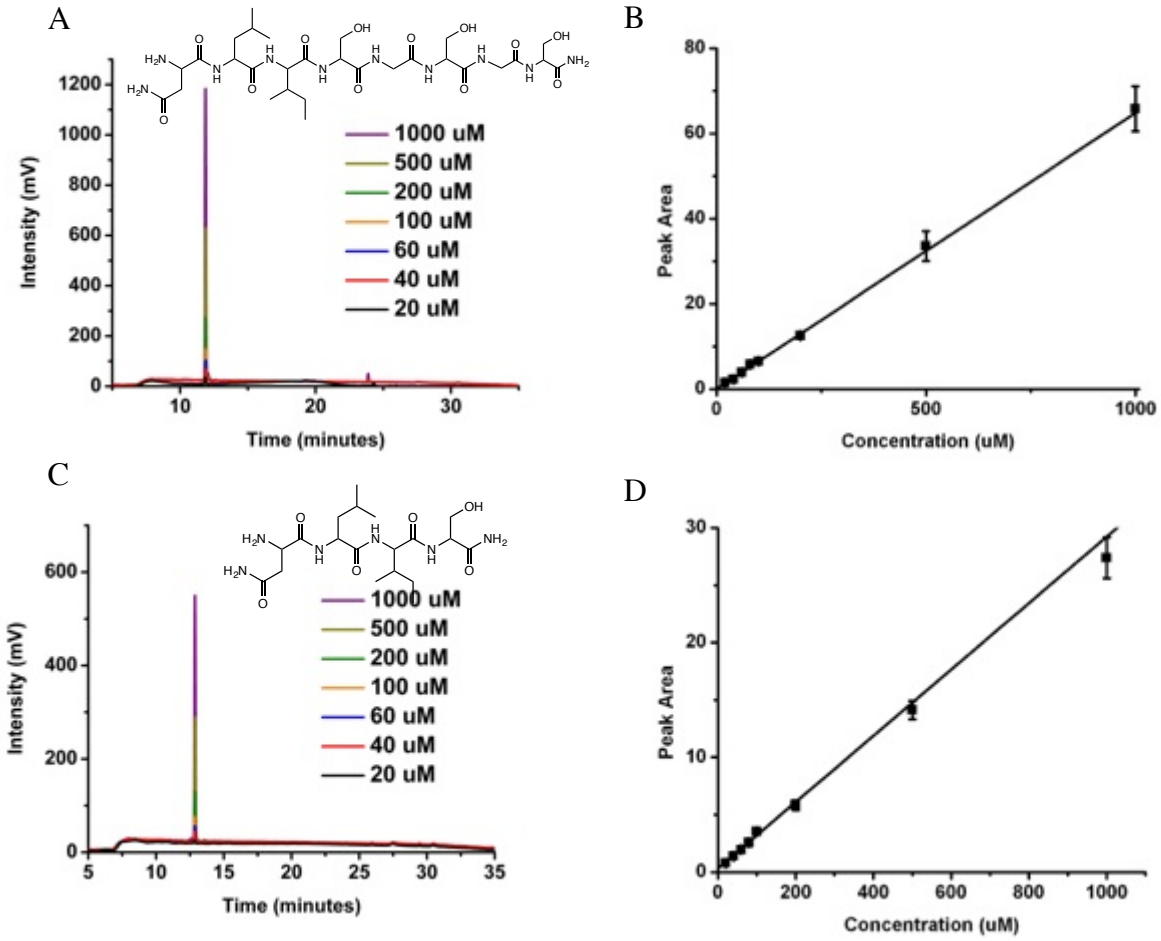

Figure S41. Standard curve for conversion of peak area to concentration.

(A) RF-HPLC trace in 10-80% buffer B of the different concentrations standard QLISGSGS.
(B) Standard curve generated from peak area of each concentration for QLISGSGS.
(C) RF-HPLC trace in 10-80% buffer B of the different concentrations standard QLIS.
(D) Standard curve generated from peak area of each concentration for QLIS.

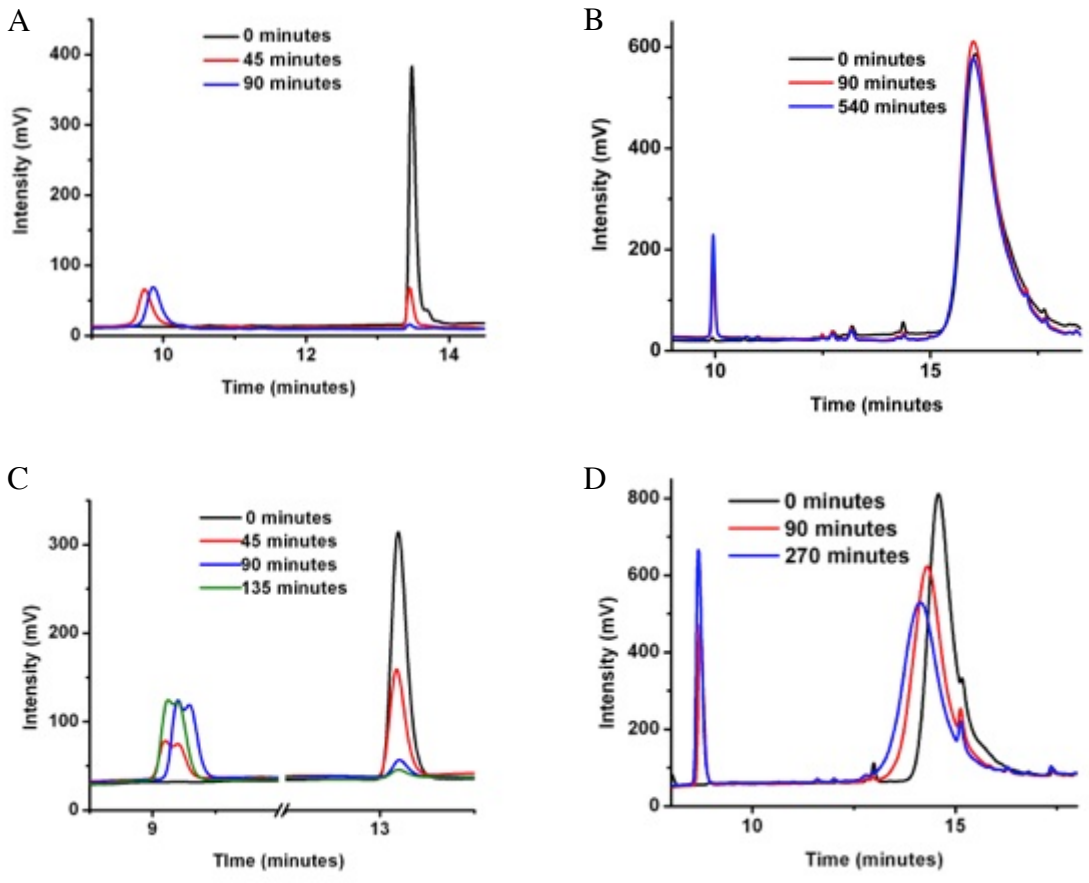

Figure S42. Trypsin cleavage of **38**, $\mathbf{38}_{21}$, **39**, and $\mathbf{39}_{19}$.

(A) RP-HPLC trace of trypsin cleavage of **38** in 10-80% buffer B over 30 minutes.
(B) RP-HPLC trace of trypsin cleavage of $\mathbf{38}_{21}$ in 10-80% buffer B over 30 minutes.
(C) RP-HPLC trace of trypsin cleavage **39** in 10-80% buffer B over 30 minutes.
(D) RP-HPLC trace of trypsin cleavage of $\mathbf{39}_{19}$ in 10-80% buffer B over 30 minutes.

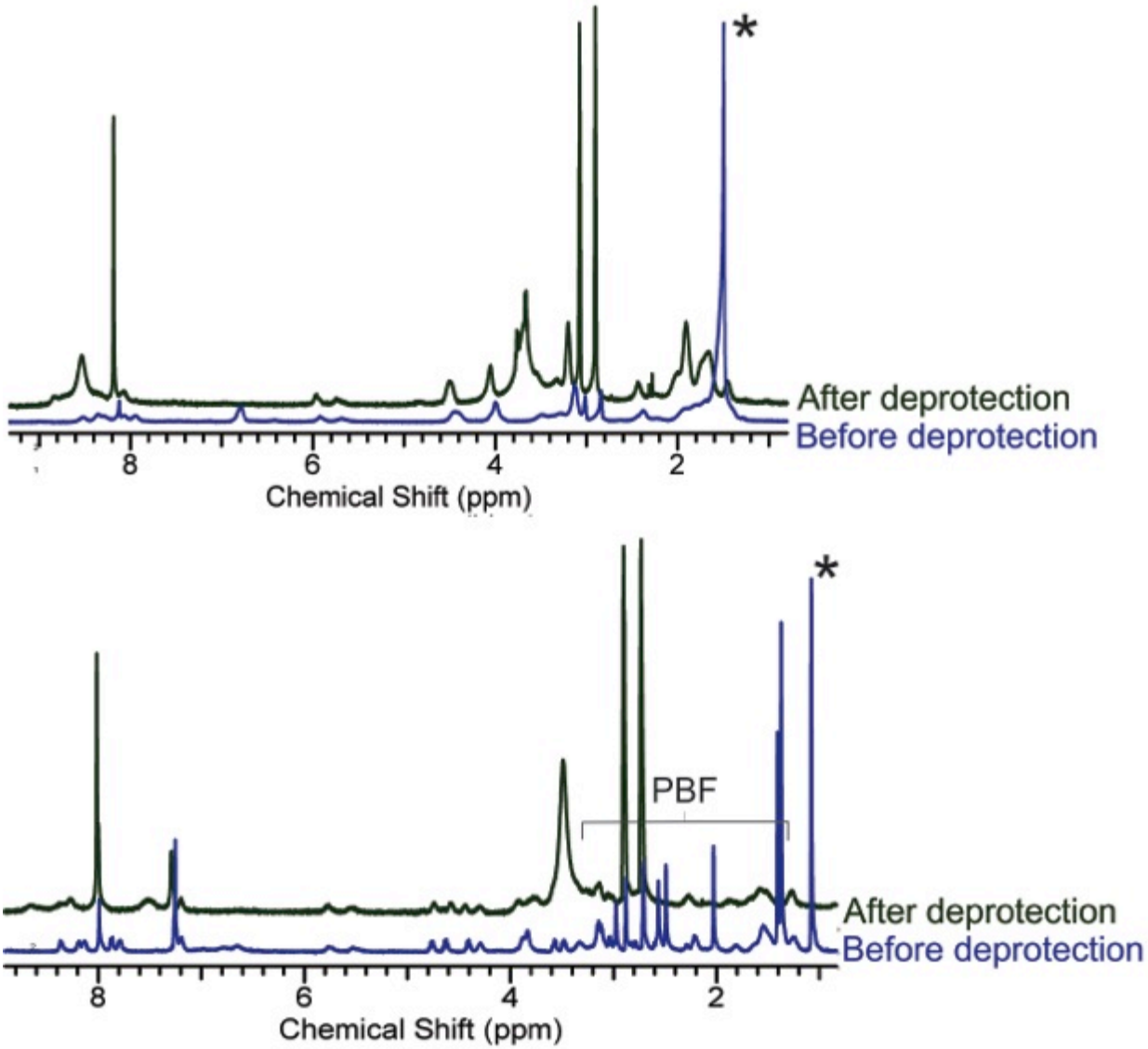

Figure S43. Characterization of deprotections of the polymers of NorGKGKGK and NorGGRGDSF. * denotes the *tert*-butyl group protons protecting lysine, serine and aspartic acid and the brackets denotes the PBF protons which protecting the arginine.

(A) ^{1}H NMR of NorGKGKGK before and after polymerization where the *tert*-butyl group is denoted by an *.

(B) ^{1}H NMR of NorGGRGDSF before and after polymerization where the *tert*-butyl group is denoted by an *, and the PBF group is denoted by a bracket.

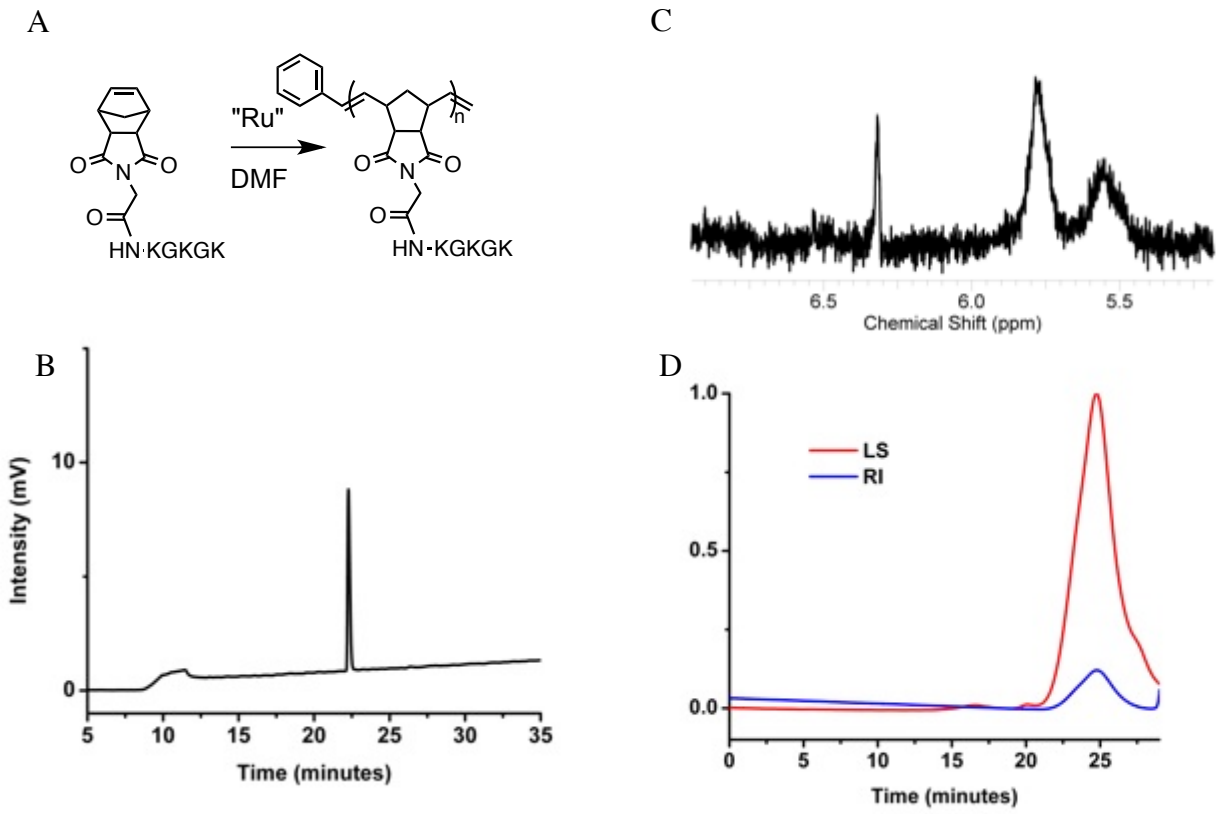

Figure S44. Polymerization and analysis of Norbornene-GKGKGK (**32**)

(A) Monomer and polymer structure
(B) RP-HPLC trace of monomer in 0-35% buffer B, retention time 23 minutes.
ESI-MS: Mass calc 718.4; Mass obs 719.8
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n = 424,000 g/mol, PDI = 1.01

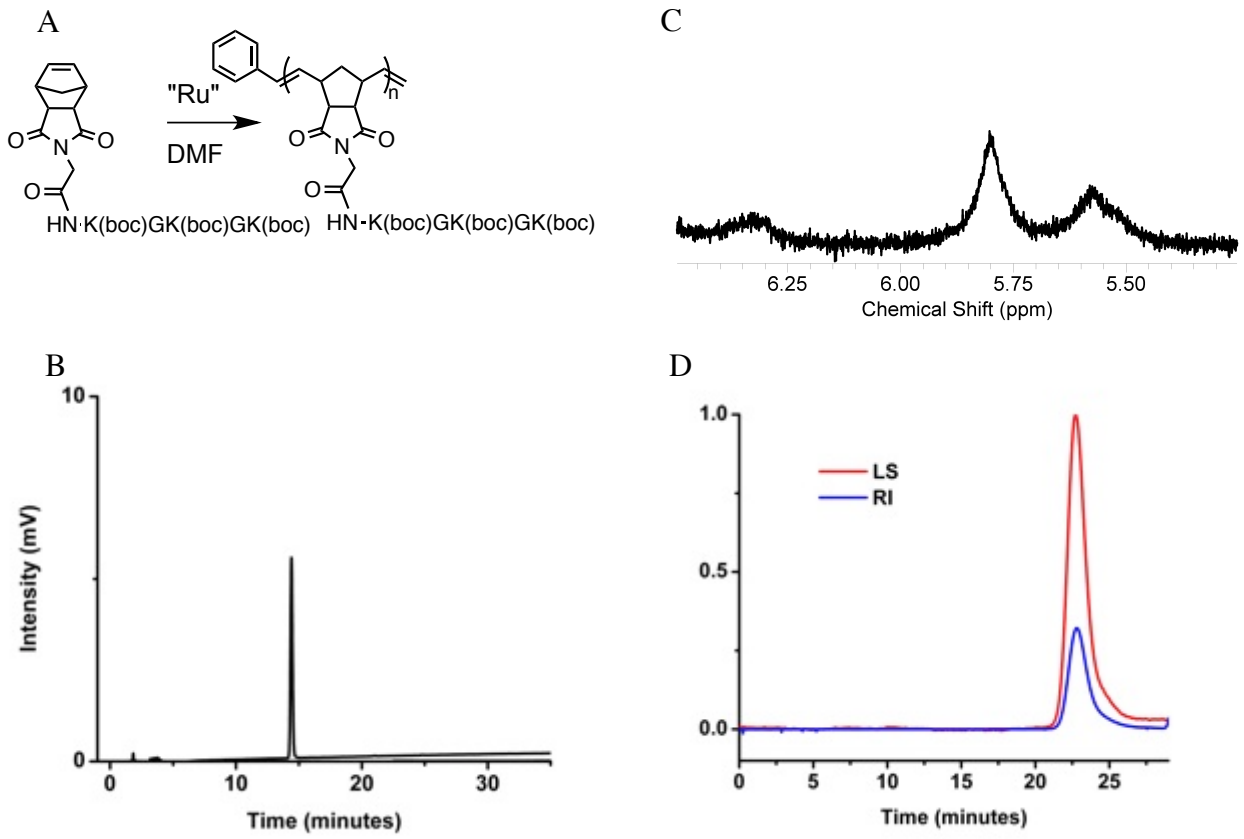

Figure S45. Polymerization and analysis of Norbornene-GK(boc)GK(boc)GK(boc) (**34**)

(A) Monomer and polymer structure
(B) RP-HPLC trace of monomer in 40-70% buffer B, retention time 15 minutes.
ESI-MS: Mass calc 1018.6; Mass obs 1020.0
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n = 11,200 g/mol, PDI = 1.01

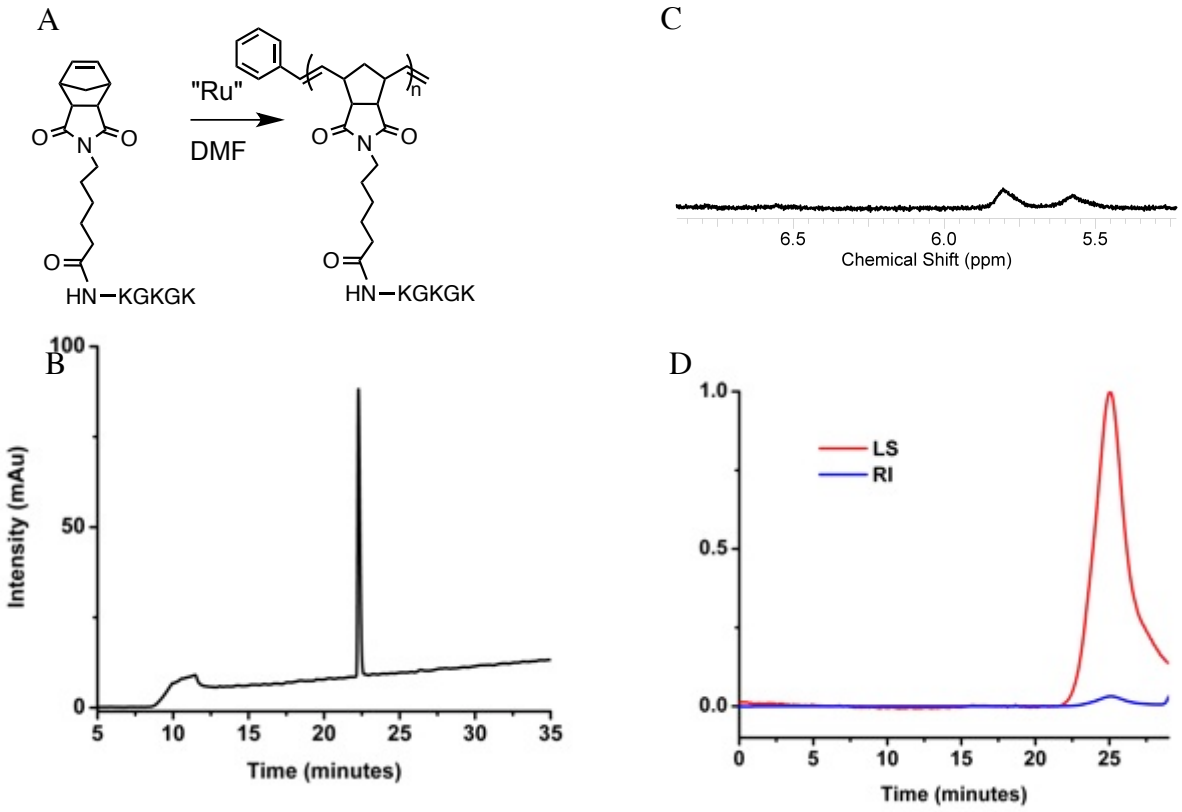

Figure S46. Polymerization and analysis of Norbornene-AhaKGKGK (**33**)

(A) Monomer and polymer structure
(B) RP-HPLC trace of monomer in 0-40% buffer B, retention time minutes. ESI-MS: Mass calc 774.5; Mass obs 775.9
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n = 286,000 g/mol, PDI = 1.01

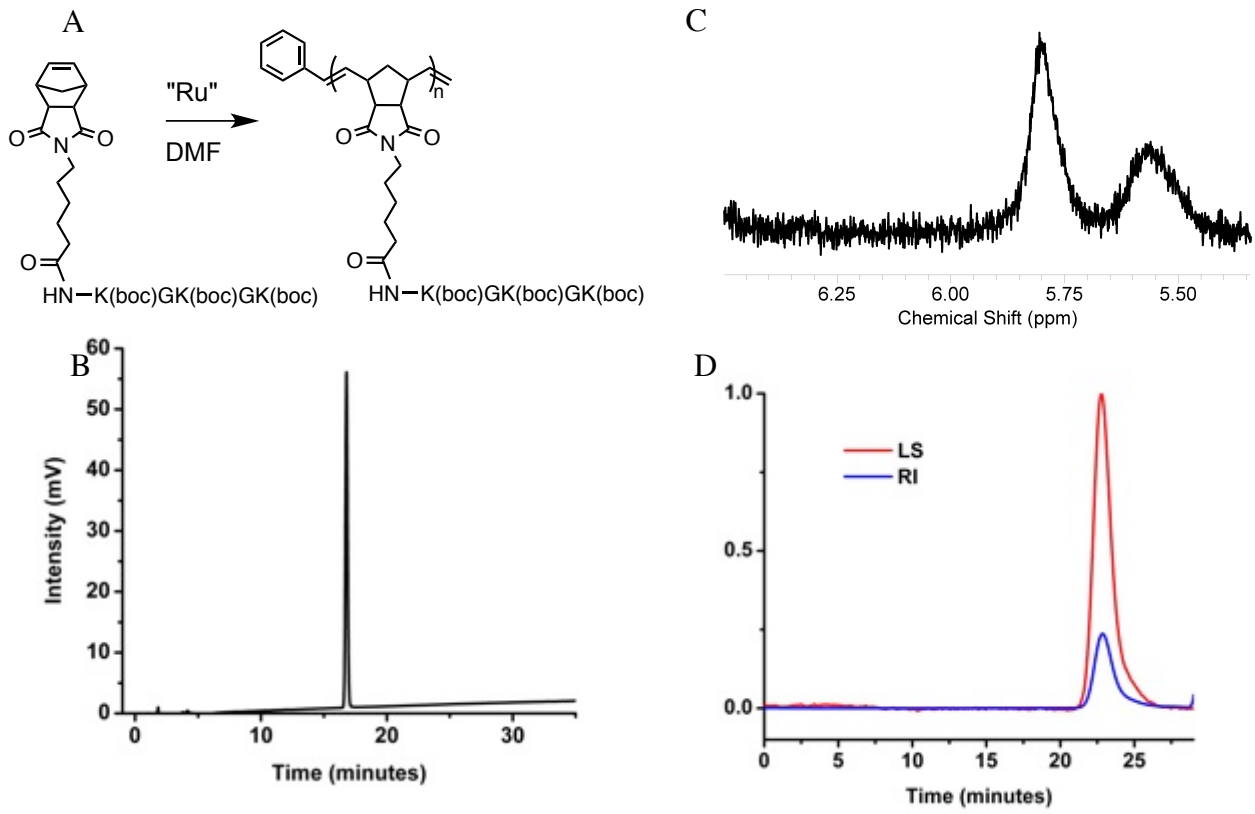

Figure S47. Polymerization and analysis of Norbornene-AhaGK(boc)GK(boc)GK(boc) (**35**)

(A) Monomer and polymer structure
(B) RP-HPLC trace of monomer in 40-70% buffer B, retention time 17 minutes.
ESI-MS: Mass calc 1074.6 ; Mass obs 1076.0
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n = 9,660 g/mol, PDI = 1.01

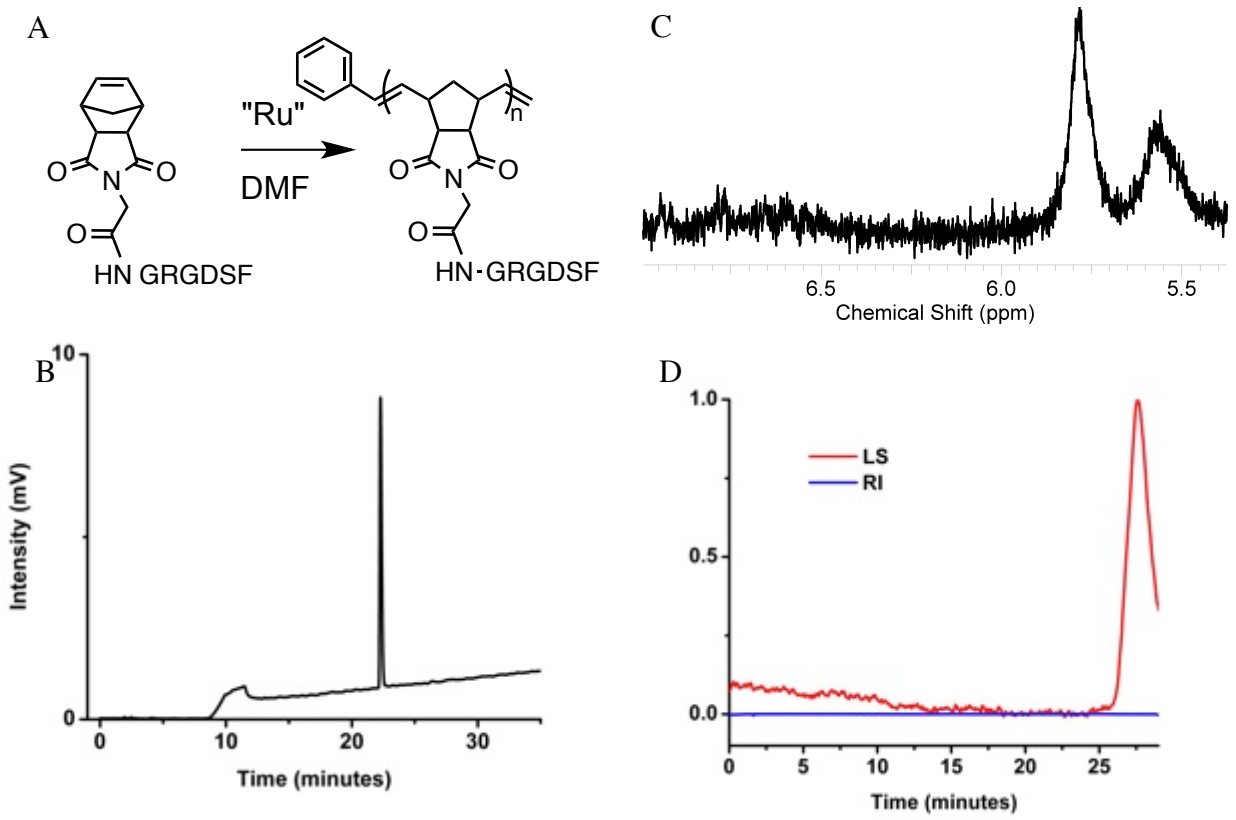

Figure S48. Polymerization and analysis of Norbornene-GGRGDSF

(A) Monomer and polymer structure
(B) RP-HPLC trace of monomer in 10-50% buffer B, retention time 22 minutes.
ESI-MS: Mass calc 839.3 ; Mass obs 840.6
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer.

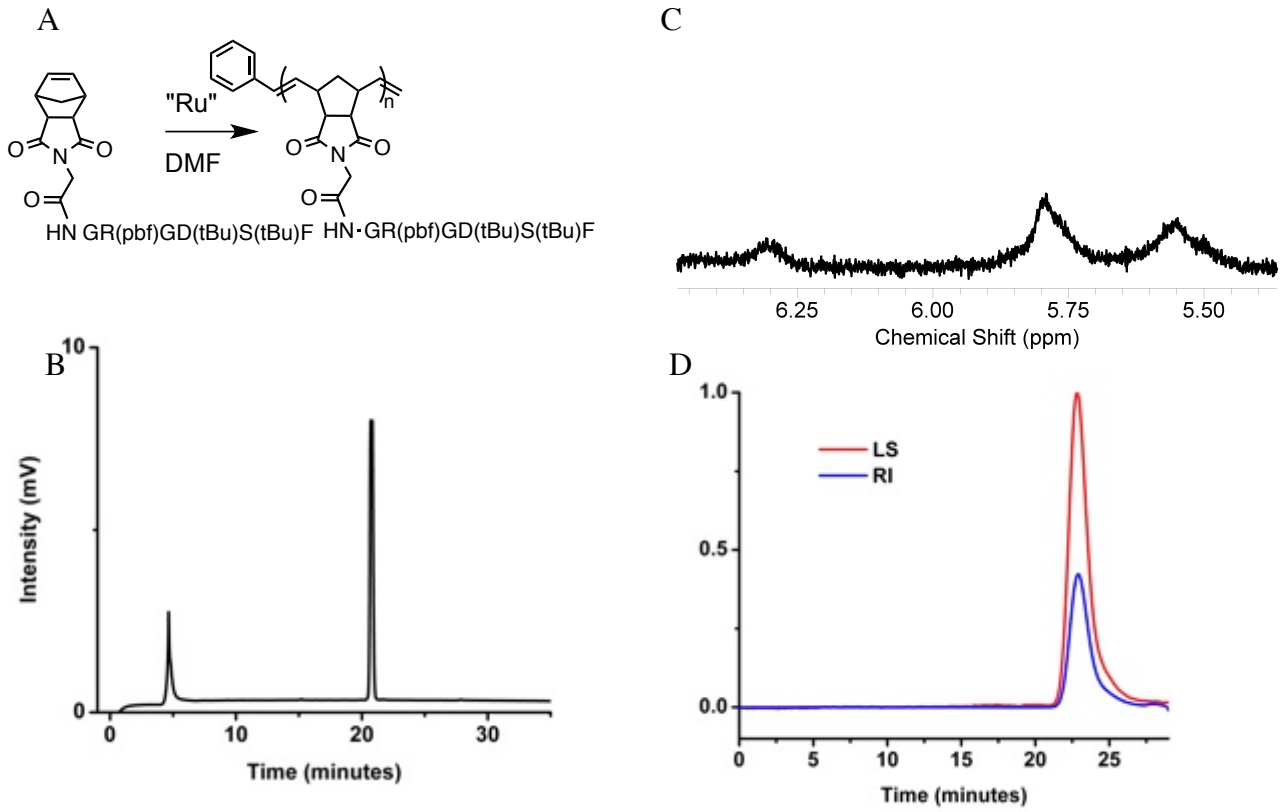

Figure S49. Polymerization and analysis of Norbornene-GGR(Pbf)GD(tBu)S(tBu)F

(A) Monomer and polymer structure
(B) RP-HPLC trace of monomer in 40-70% buffer B, retention time 20 minutes. ESI-MS: Mass calc 1203.5; Mass obs 1205.1
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS: M_n =15,600 g/mol, PDI = 1.01

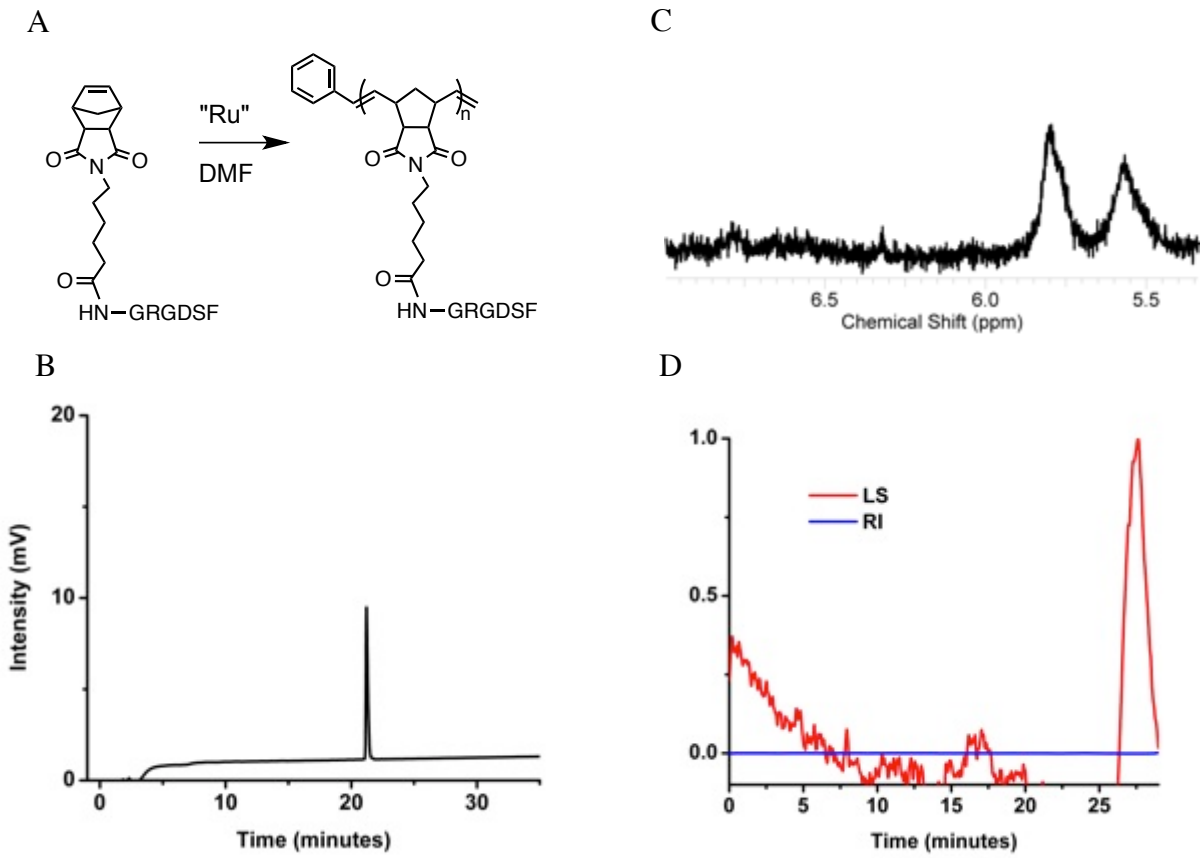

Figure S50. Polymerization and analysis of Norbornene-AhaGRGDSF

(A) Monomer and polymer structure:
(B) RP-HPLC trace of monomer in 40-70% buffer B, retention time 21 minutes.
ESI-MS: Mass calc 895.4; Mass obs 896.6
(C) ^{1}H NMR following monomer polymerization: M:I = 20:1
(D) SEC-MALS data of polymer. SEC-MALS

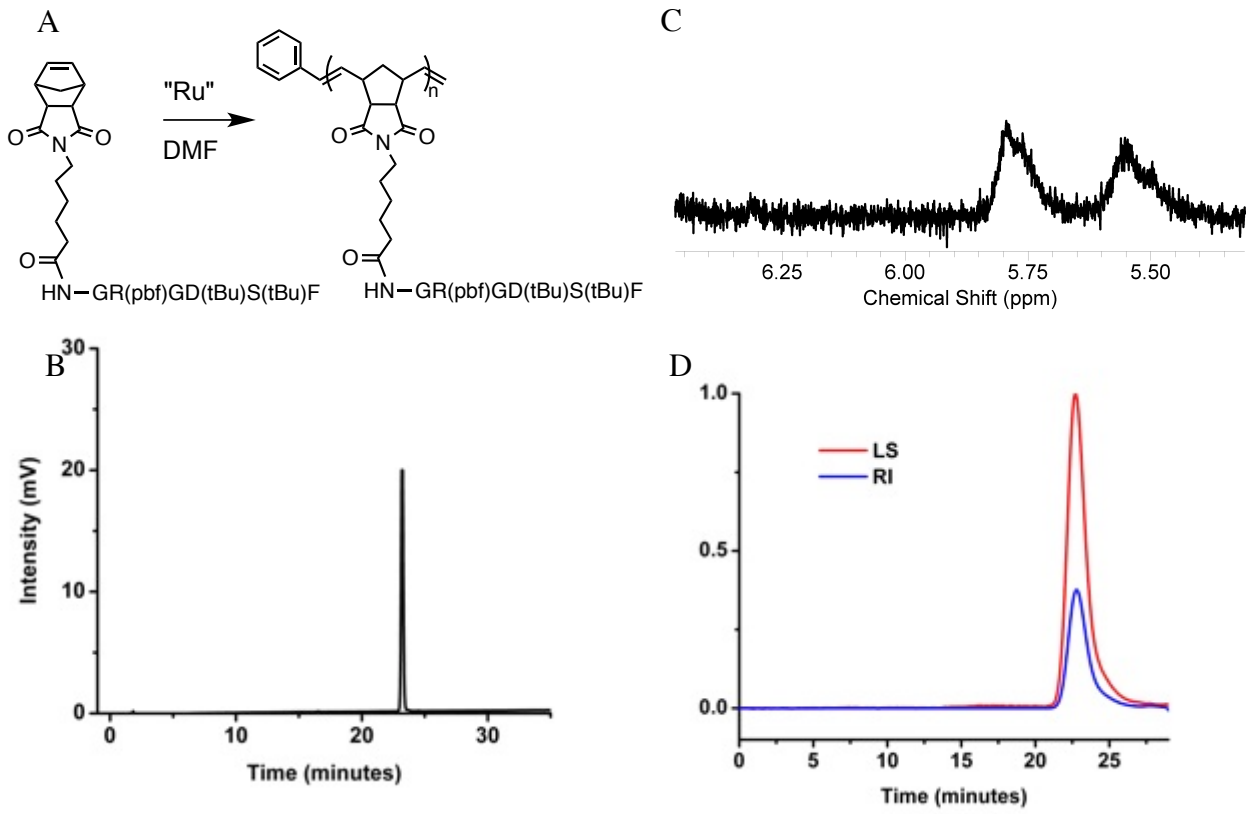

Figure S51. Polymerization and analysis of Norbornene-AhaGR(Pbf)GD(tBu)S(tBu)F

(A) Monomer and polymer structure
(E) RP-HPLC trace of monomer in 40-70% buffer B, retention time 24 minutes.
ESI-MS: Mass calc 1259.6; Mass obs 1262.0
(F) ^{1}H NMR following monomer polymerization: M:I = 20:1
(G) SEC-MALS data of polymer. SEC-MALS: M_n =16,300 g/mol, PDI = 1.01

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2. Sanford, M. S., Love, J. A., and Grubbs, R. H. *Organometallics*, 2011, **20**, 5314-5318

3. Patel, P. R., Kiser, R. C., Lu, Y. Y., Fong, E., Ho, W. C., Tirrell, D. A. and Grubbs, R. H. . *Biomacromolecules,* 2012, **13**, 2546.