

Ruthenium-catalyzed cascade metathetical cyclopolymerization (CMCP) of bisnorbornenes with flexible linkers

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Supporting Information

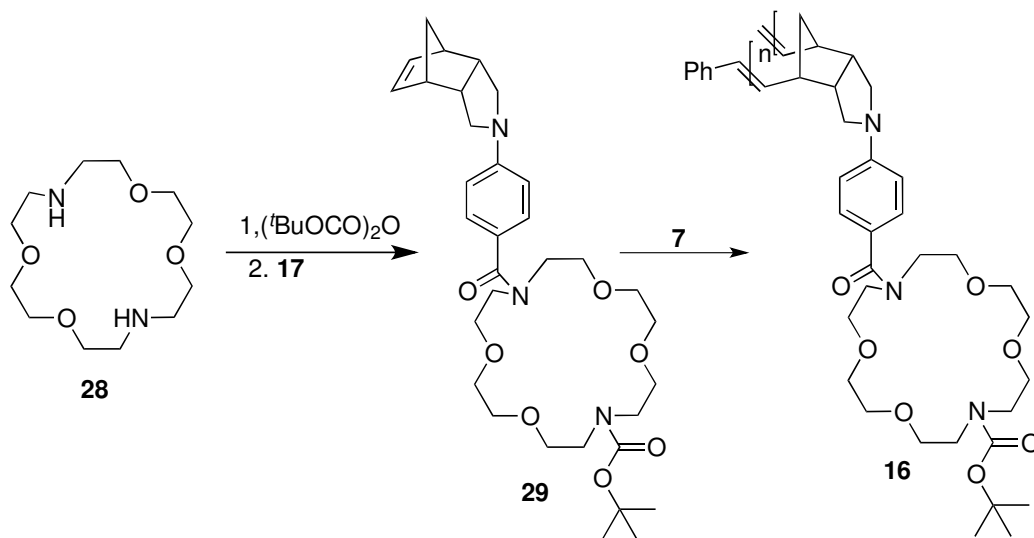
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Additional Experimental Section

General. Melting points were uncorrected. All ^1H and ^{13}C NMR spectra were recorded on a Varian 400 Unity Plus spectrometer (400 MHz) or a Bruker Avance-500 MHz or an AV III 800 MHz FT-NMR spectrometer at ambient temperature using CDCl_3 as solvent and TMS as the internal standard. The chemical shifts in ^{13}C NMR spectra was calibrated using the peak of CDCl_3 at δ 77.0 ppm as the reference. All air-sensitive manipulations were performed under nitrogen or in a drybox. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. Dichloromethane (DCM) was purged with nitrogen, passed through activated alumina, and stored over molecular sieves in a nitrogen atmosphere. Benzaldehyde was distilled and stored under nitrogen. High resolution mass spectrometry was obtained by employing a Jeol-JMS-700 mass spectrometer using the FAB method with a 3-nitrobenzyl alcohol matrix.



Monomer 29. To a solution of **28** (520 mg, 2 mmol) in dioxane (5 mL) was added a solution of di-tert-butyl dicarbonate (650 mg, 3 mmol) in dioxane (5 mL). The mixture was stirred for 10 h, and then evaporated in vacuo. To the residue was added Et_3N (300 mg, 3 mmol) in DCM (20 mL) and **17** (550 mg, 2 mmol) in DCM (20 mL) at 0 °C. The mixture was gradually warmed to rt and stirred for 10 h, poured into water (100 mL) and extracted with DCM (50 mL \times 2). The organic layer was washed

with brine (100 mL×2), dried (MgSO₄), filtered, and evaporated in vacuo. The residue was chromatographed on silica gel (hexane/DCM 1/5) to afford **29** as an oil (420 mg, 35%): ¹H NMR (400 MHz, CDCl₃) δ 1.44 (s, 9 H), 1.51 (d, *J* = 8.4 Hz, 1 H), 1.60 (d, *J* = 8.4 Hz, 1 H), 2.80-2.89 (m, 2 H), 2.97 (br, 2 H), 3.02-3.10 (m, 2 H), 3.20-3.27 (m, 2 H), 3.46-3.54 (m, 4 H), 3.54-3.64 (m, 14 H), 3.65-3.76 (m, 8 H), 6.15 (t, *J* = 1.8 Hz, 2 H), 6.36 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 28.5, 45.5, 46.6, 47.9, 48.1, 50.5, 52.1, 69.9, 70.4, 70.5, 79.5, 110.9, 122.4, 128.4, 135.6, 148.1, 155.2, 172.6; HRMS (FAB). Calcd. C₃₃H₄₉N₃O₇: 599.3571, Found: 599.3564.

Polymer 16. To a solution of **29** (200 mg, 0.3 mmol) in DCM (5 mL) stirred under N₂ was added **7** (27 mg, 0.03 mmol) in DCM (2 mL). After stirring for 1 h at rt, ethyl vinyl ether (2 mL) was added and the mixture was stirred for 10 min. The resulting solution was concentrated and the polymer **16** was precipitated in Et₂O (30 mL) as a white solid (150 mg, 75%): ¹H NMR (400 MHz, CDCl₃) δ 1.25-1.65 (br, 10 H), 1.65-1.95 (br, 1 H), 2.66-2.85 (br, 2 H), 2.85-3.05 (br, 2 H), 3.05-3.38 (br, 4 H), 3.40-4.00 (br, 24 H), 5.30-5.60 (br, 2 H), 6.35-6.70 (br, 2 H), 7.18-7.50 (br, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 28.4, 36.2, 36.5, 44.8, 46.4, 46.7, 47.8, 48.0, 49.6, 69.8, 70.2, 70.4, 79.3, 111.7, 115.1, 123.3, 125.7, 126.8, 128.2, 130.3, 130.6, 131.4, 131.7, 137.0, 138.7, 148.6, 155.0, 172.2; GPC (CHCl₃) M_n = 5,200, PDI = 1.2.

Polymer 18. Under N₂, a solution of **16** (200 mg, 0.3 mmol) and trifluoroacetic acid (1 mL) in DCM (5 mL) was stirred at rt for 5 h, poured into water (50 mL), neutralized with K₂CO₃ (1 M) and extracted with DCM (50 mL×2). The organic layer was washed with brine (100 mL), dried (MgSO₄), filtered, and evaporated in vacuo to give the crude deprotected polymer which was used for the next reaction without further purification.

To a solution of the above residue and Et₃N (100 mg, 1 mmol) in DCM (5 mL) at 0 °C was added a solution of **17** (270 mg, 1 mmol) in DCM (5 mL). The reaction was gradually warmed to rt and stirred for 10 h. The mixture was poured into water (100 mL), extracted with DCM (50 mL×2). The organic layer was separated, washed with

brine (100 mL×2), dried (MgSO₄) and filtered. The solvent was removed in vacuo to give the residue which was treated again with **17** in a manner similar to that described above to give **18** (precipitated from 50 mL of Et₂O) as a gray solid (150 mg, 70 %): ¹H NMR (500 MHz, CDCl₃) δ 1.30-1.48 (br, 1 H), 1.48-1.58 (br, 1 H), 1.58-1.66 (br, 1 H), 1.70-1.95 (br, 1 H), 2.64-2.86 (br, 2 H), 2.86-3.00 (br, 6 H), 3.00-3.10 (br, 2 H), 3.10-3.38 (br, 6 H), 3.45-3.66 (br, 8 H), 3.66-3.92 (br, 16 H), 5.28-5.60 (br, 2 H), 6.08-6.20 (br, 2 H), 6.28-6.40 (br, 2 H), 6.40-6.70 (br, 2 H), 7.18-7.46 (br, 2 H); ¹³C NMR (125 MHz, CDCl₃) δ 36.6, 44.8, 45.3, 46.5, 49.7, 50.4, 52.0, 70.0, 70.5, 110.9, 111.9, 122.5, 123.6, 128.5, 131.7, 135.7, 148.3, 148.9, 172.6, 172.8; GPC (CHCl₃) M_n = 6,400, PDI = 1.2.

Polymer 19. To a solution of **18** (20 mg, 3×10⁻² mmol) in DCM (70 mL) stirred under N₂ atmosphere was treated with a solution of **7** (3 mg, 0.003 mmol) in DCM (2 mL). After stirring for 2 h at rt, ethyl vinyl ether (5 mL) was added and the mixture was stirred for 10 min. The resulting solution was concentrated and the polymer **19** was precipitated in Et₂O (30 mL) as a gray solid (19 mg, 95 %): ¹H NMR (500 MHz, CDCl₃) δ 1.10-1.65 (br, 2 H), 1.65-2.10 (br, 2 H), 2.50-3.35 (br, 16 H), 3.35-4.20 (br, 24 H), 5.20-5.96 (br, 4 H), 6.15-6.90 (br, 4 H), 7.00-7.70 (br, 4 H); ¹³C NMR (125 MHz, CDCl₃) δ 37.1, 37.6, 46.4, 49.6, 70.4, 112.0, 123.6, 125.9, 128.5, 131.8, 148.7, 172.6; GPC (CHCl₃) M_n = 7,100, PDI = 1.2.

Polymer 15d. In a manner similar to that described for **15** described in the Experimental Section in the text, hydrolysis of **19** (0.03 mmol of ester group) yielded **15d** as a yellowish solid (89 %): ¹H NMR (400 MHz, CDCl₃) δ 1.12-1.50 (br, 4 H), 1.70-1.90 (br, 1 H), 2.60-2.80 (br, 2 H), 2.80-3.00 (br, 2 H), 3.10-3.60 (br, 4 H), 4.10-4.50 (br, 2H), 5.10-5.60 (br, 2 H), 6.30-6.70 (br, 2 H), 7.70-8.10 (br, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.9, 36.6, 36.8, 45.1, 46.1, 49.6, 49.8, 60.4, 111.6, 117.5, 126.2, 127.4, 130.8, 132.0, 137.4, 139.0, 150.9, 167.1; GPC (CHCl₃) M_n = 2,900, PDI = 1.2.

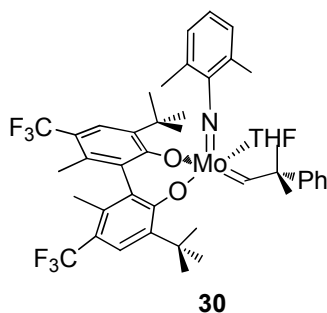
Polymer 21. To a solution of **20** (30 mg, 0.10 mmol) in DCM (20 mL) stirred under N₂ atmosphere was treated with a DCM solution (2 mL) of **7** of different amounts.

After stirring for 2 h at rt, ethyl vinyl ether (2 mL) was added and the mixture was stirred for 10 min. The resulting solution was concentrated and the polymer **21** was precipitated in methanol (30 mL) as a white solid: ^1H NMR (400 MHz, CDCl_3) δ 1.22-1.53 (br, 4 H), 1.55-2.00 (br, 1 H), 2.56-2.78 (br, 2 H), 2.80-3.80 (br, 2 H), 3.02-3.48 (br, 4 H), 4.15-4.48 (br, 2 H), 5.22-5.56 (br, 2 H), 6.38-6.62 (br, 2 H), 7.78-8.00 (br, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.4, 35.7, 36.1, 44.5, 44.8, 46.4, 46.6, 46.8, 49.2, 49.4, 60.0, 111.4, 117.3, 126.0, 128.5, 131.2, 131.8, 150.8, 167.0;

21a (10% mol of **1**) (29 mg, 97 %): GPC (CHCl_3) $M_n = 3,700$, PDI = 1.3.

21b (5% mol of **1**) (25 mg, 83 %): $M_n = 6,300$, PDI = 1.3.

21c (2% mol of **1**) (26 mg, 87 %): $M_n = 14,000$, PDI = 1.2.



Polymer 22. To a DCM solution (20 mL) of **20** (100 mg, 0.35 mmol) was added a DCM solution (2 mL) of **30** (15 mg, 17.5 μmol) in a dry box. The mixture was stirred for 2 h at rt, after which, benzaldehyde (200 μL , 2.0 μmol) was added. The mixture was stirred for an additional 1 h and then added dropwise to vigorously stirred methanol (100 mL) to give a fine white solid **22** (83 mg, 83%). The white solid polymer was isolated by filtration, rinsed with methanol, and dried in vacuo. ^1H NMR (400 MHz, CDCl_3) δ 1.20-1.57 (br, 4 H), 1.80-2.00 (br, 1 H), 2.65-3.16 (br, 4 H), , 3.20-3.45 (br, 4 H), 4.10-4.42 (br, 2 H), 5.20-5.38 (br, 2 H), 6.32-6.60 (br, 2 H), 7.68-8.02 (br, 2 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.6, 39.1, 40.2, 47.6, 49.5, 60.3, 111.6, 118.0, 131.4, 132.4, 150.7, 167.0. GPC (THF) $M_n = 8,400$, PDI = 1.2.

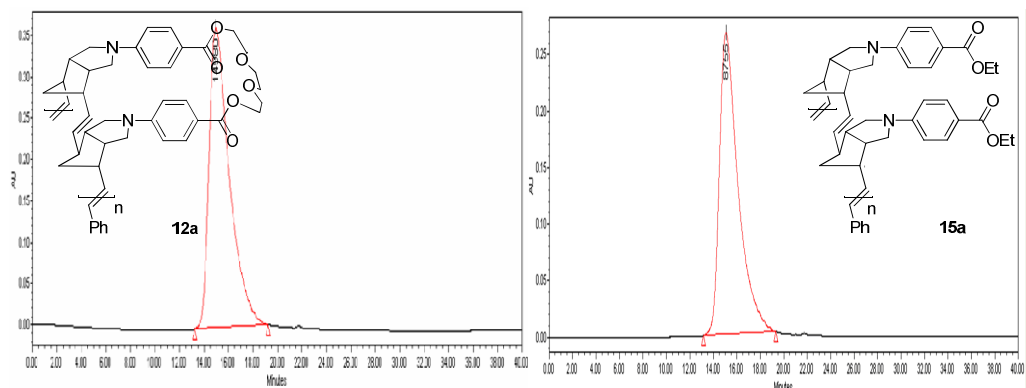
Polymer 23a. A solution of **15c** (51 mg, 0.19 mmol) and *p*-tosylhydrazide (0.55g, 3.0 mmol) in PhCl (8 mL) was stirred under nitrogen at 120 $^\circ\text{C}$ for 2 h and filtered. The hot filtrate was poured into methanol (25 mL). The mixture was centrifuged to

collect the precipitate, which was washed several times with methanol and dried under vacuum to yield **23a** (42 mg, 80%) : ^1H NMR (400 MHz, CDCl_3) δ 0.88-1.02 (br, 1 H), 1.05-1.56 (br, 4 H), 1.85-2.12 (br, 3 H), 2.80-3.00 (br, 2 H), 3.10-3.50 (br, 4 H), 3.66-4.00 (br, 3H), 6.35-6.60 (br, 2 H), 7.79-8.00 (br, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.6, 30.9, 37.1, 41.7, 45.2, 48.7, 60.2, 111.4, 117.2, 131.1, 150.8, 166.8. GPC (CHCl_3) M_n =5,200, PDI =1.2.

Polymer 23b. In a manner similar to that described above, reaction of **21b** (54 mg, 0.19 mmol) and *p*-tosylhydrazide (0.55g, 3.0 mmol) yielded **23b** (47 mg, 89%): ^1H NMR (400 MHz, CDCl_3) δ 0.81-1.62 (br, 8 H), 1.78-2.20 (br, 3 H), 2.69-3.00 (br, 2 H), 3.02-3.48 (br, 4 H), 4.10-4.46 (br, 2H), 6.32-6.70 (br, 2 H), 7.76-8.00 (br, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.6, 31.0, 37.1, 41.7, 45.2, 48.7, 60.1, 111.4, 117.2, 131.1, 150.8, 166.8. GPC (CHCl_3) M_n =6,900, PDI =1.1.

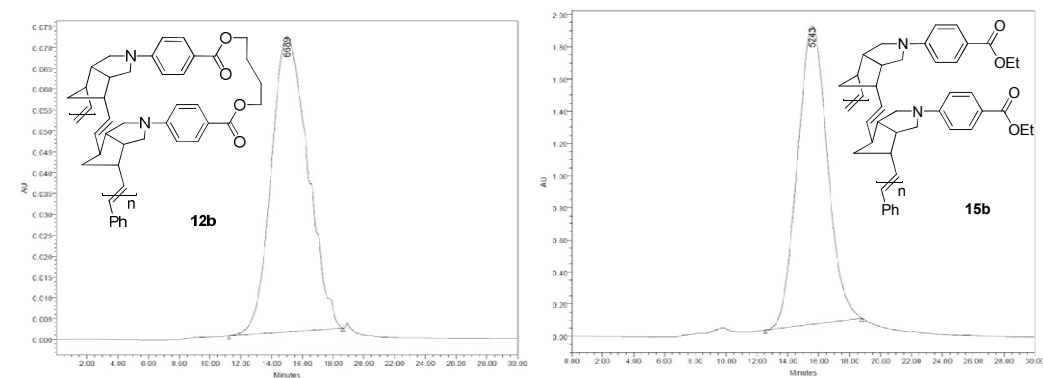
Polymer 23c. In a manner similar to that described above, reaction of **22** (85 mg, 0.30 mmol) and *p*-tosylhydrazide (0.55g, 3.0 mmol) yielded **23c** (72 mg, 85%): ^1H NMR (400 MHz, CDCl_3) δ 0.80-1.62 (br, 8 H), 1.76-2.19 (br, 3 H), 2.67-3.00 (br, 2 H), 3.02-3.48 (br, 4 H), 4.10-4.48 (br, 2H), 6.22-6.71 (br, 2 H), 7.70-8.18 (br, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.6, 31.0, 37.1, 41.7, 45.2, 48.7, 60.1, 111.4, 117.2, 131.1, 150.8, 166.8. GPC (THF) M_n =8,300, PDI =1.2.

GPC results of polymers. GPC was performed on a Waters GPC instrument equipped with Waters 1515 HPLC pump using Waters 2487 absorbance detector. Polymer (approximately 0.5 mg) in CHCl_3 (0.1 mL) was filtered through a 0.5-micron filter and 20 μL of the sample was injected into Shodex K-803, K-802.5 columns with oven temperature at 40 $^\circ\text{C}$ using standard polystyrene samples (1.17×10^5 -996 Da) for calibration. Chloroform was used as the eluent (flow rate = 1.0 mL min^{-1}). Waters Empower HPLC/GPC network software was used for data analyses. Polymers **22** and **23c** were tested using THF as solvent. The results are shown in Figures S1.



Name	Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1 Broad	14.880			7798	9078	14980		16369	17488	1.163690

Name	Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1 Broad	15.185			6701	7798	8755		8680	9488	1.163690

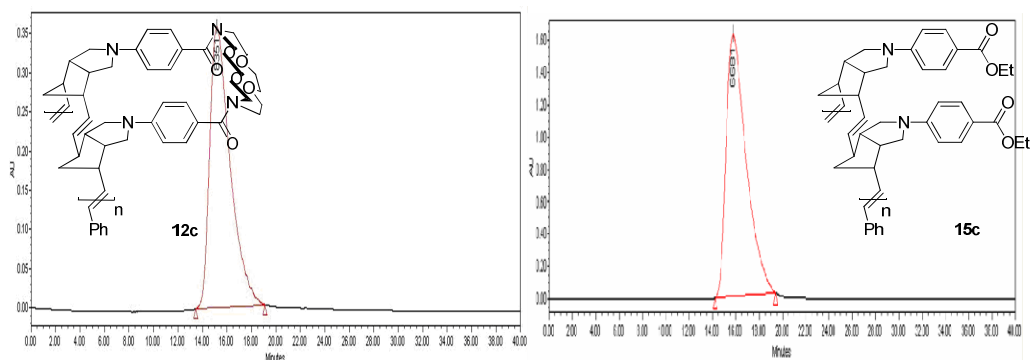


Peak Results

Name	RT	Area	Height	Mn (Daltons)	Mw (Daltons)	Polydispersity
1 Broad	15.000	117.60805	70881	5269	6927	1.314051

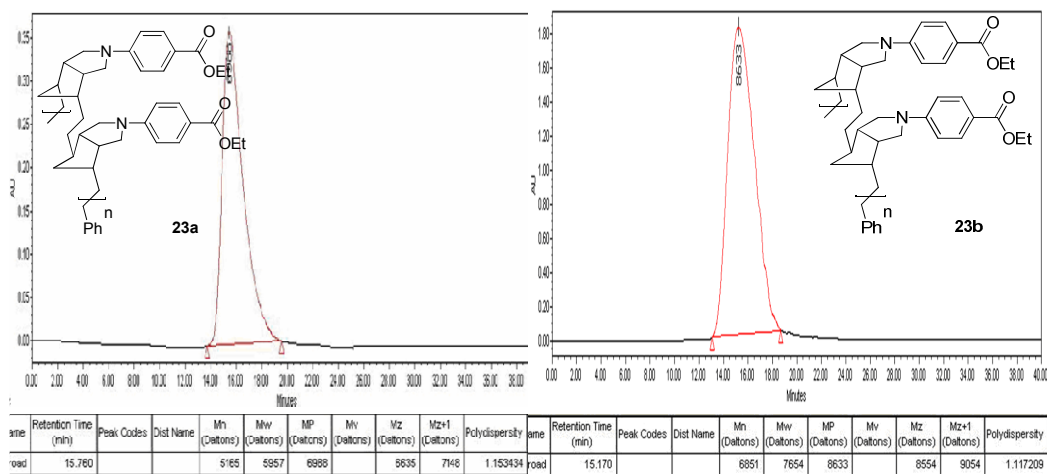
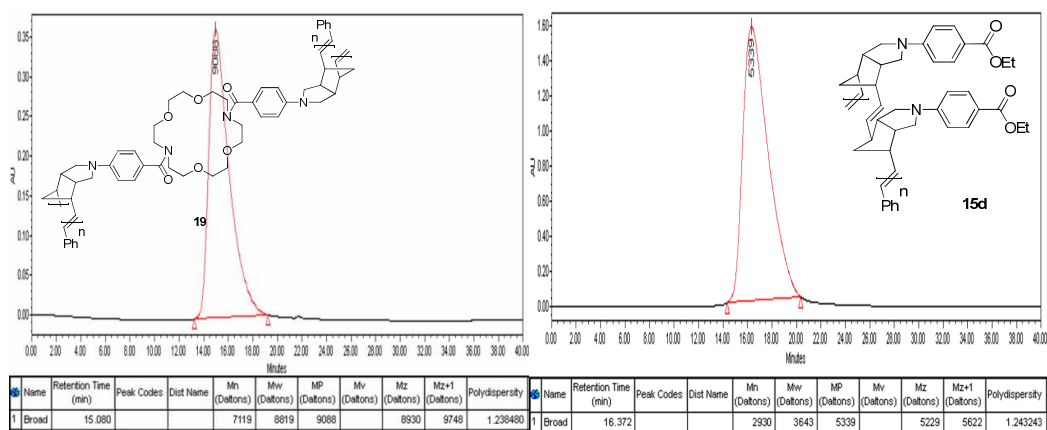
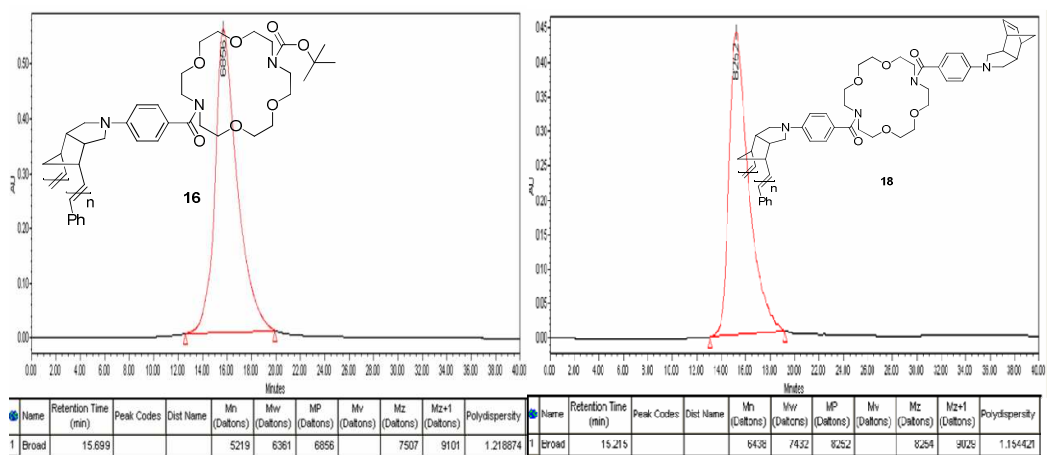
Peak Results

Name	RT	Area	Height	Mn (Daltons)	Mw (Daltons)	Polydispersity
1 Broad	15.576	251178930	1803900	4911	5529	1.109241



Name	Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1 Broad	15.209			6516	8155	8381		8254	8954	1.251536

Name	Retention Time (min)	Peak Codes	Dist Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1 Broad	15.754			4977	5805	6681		6420	6699	1.160519



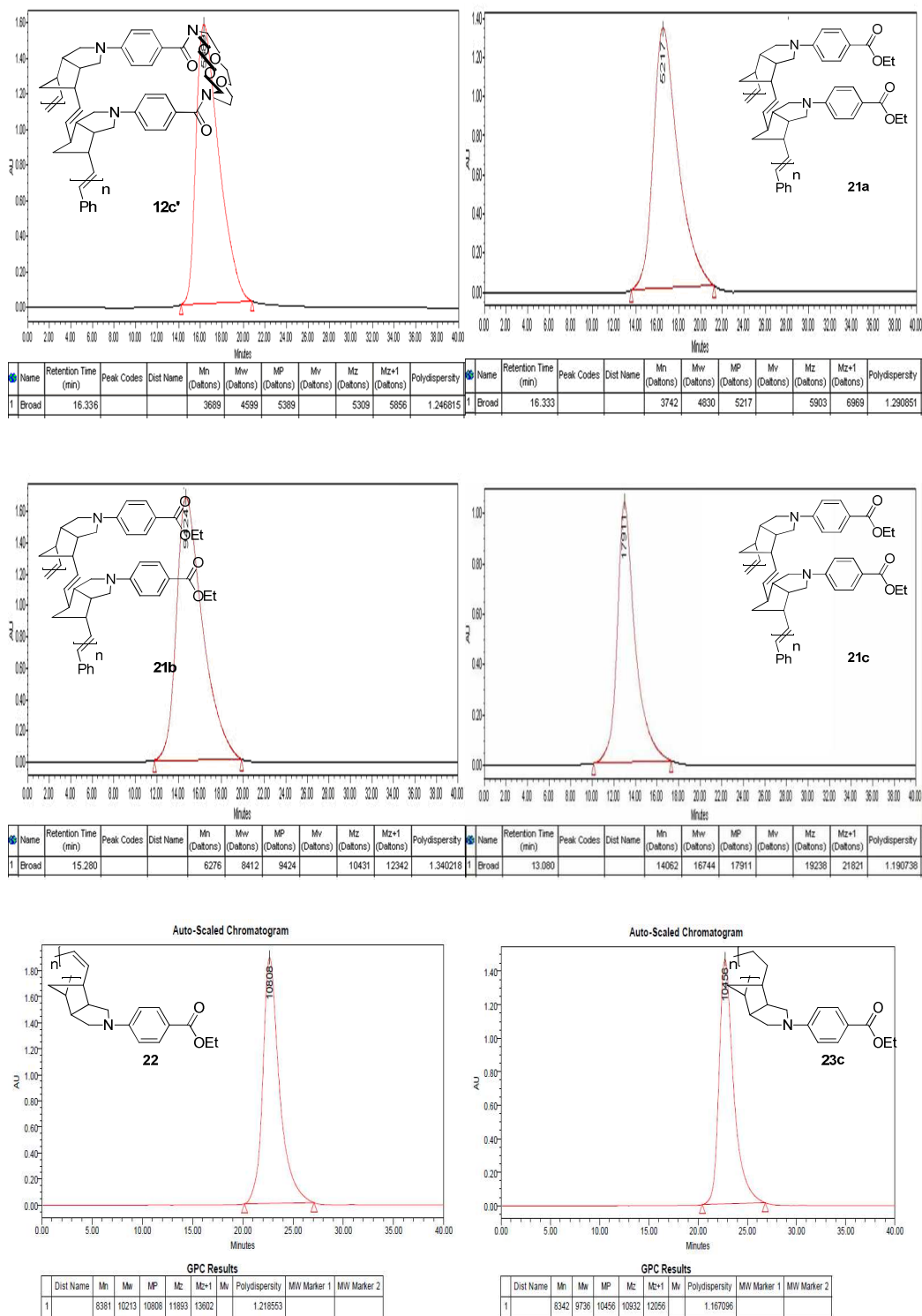


Figure S1. GPC chromatograms for polymers **12a-c**, **12c'**, **15a-d**, **16**, **18**, **19**, **21a-c**, **22** and **23a-c**.

DLS data.

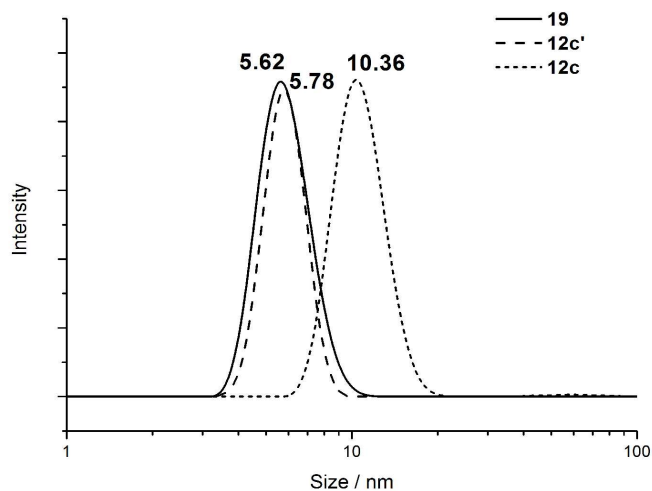


Figure S2. Hydrodynamic diameters in CHCl_3 (0.1 mM) solution of **12c** (with 9 repeat bisnorbornene units), **12c'** (with 5 repeat bisnorbornene units) and **19** analyzed by DLS.

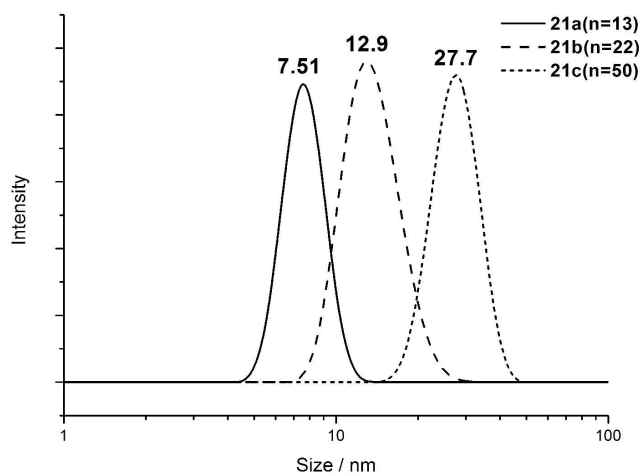


Figure S3. Hydrodynamic diameters in CHCl_3 (0.1 mM) solution of **21a**, **21b** and **21c**.

Intrinsic viscosity data

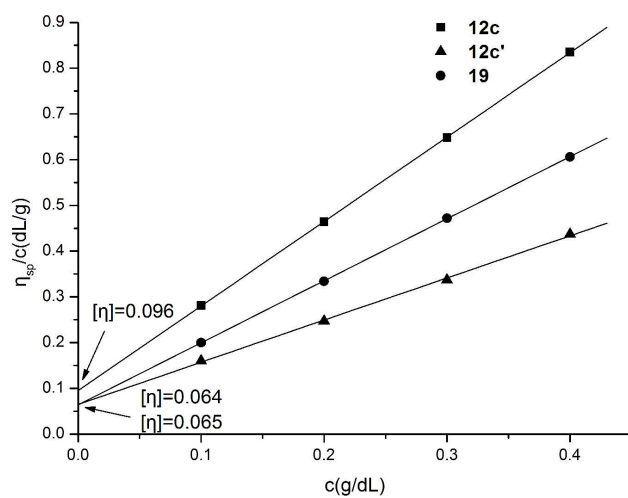


Figure S4. Intrinsic viscosity in CHCl_3 solution of **12c** (with 9 repeat bisnorbornene units), **12c'** (with 5 repeat bisnorbornene units) and **19** measured by the Ubbelohde viscometer.

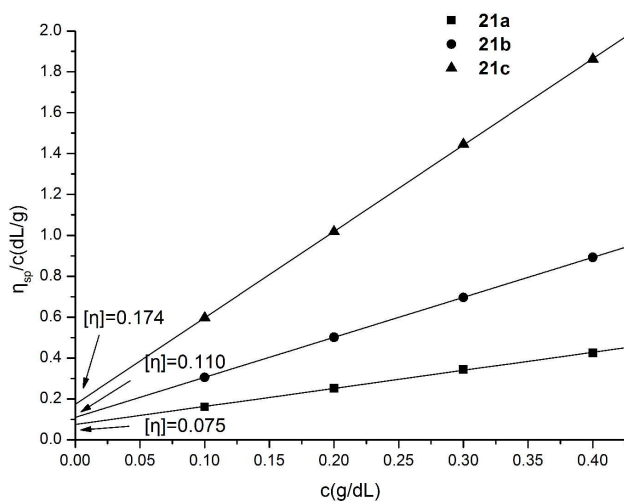


Figure S5. Intrinsic viscosity in CHCl_3 solution of **21a**, **21b** and **21c**.

¹³C NMR spectra of **22**, **21** and **15c**

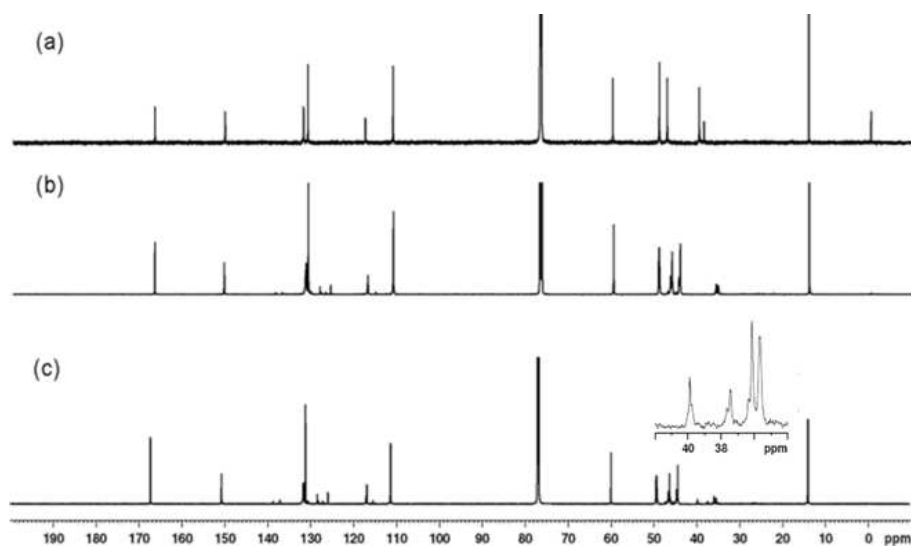


Figure S6. A comparison of the ¹³C NMR spectra of (a) **22** (b) **21** in CDCl₃ using power gate decoupling mode and (c) **15c** in CDCl₃. Inset : expanded region from δ 34-42 ppm for **15c**.

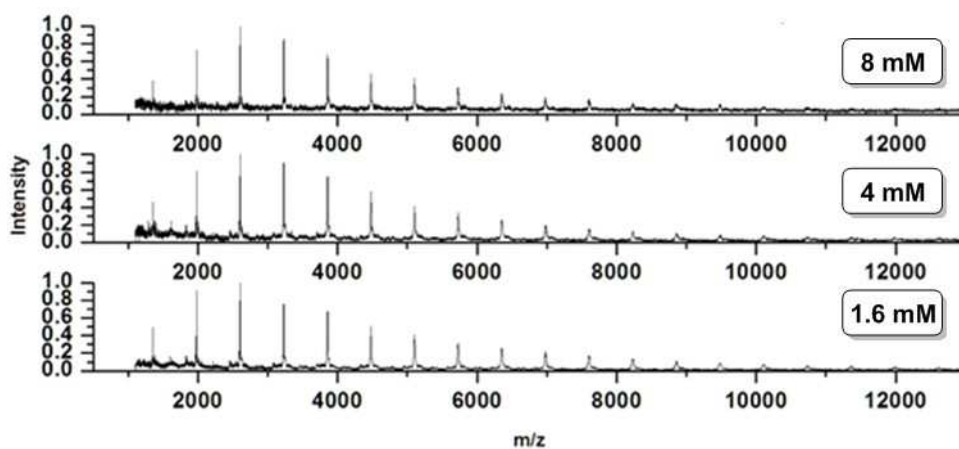


Figure S7. MALDI-TOF spectra of polybisnorbornenes **12a** obtained from CMCP of **10a** at different concentrations.

¹H and ¹³C NMR spectra of new compounds and polymers

