Supporting Information

Partial Kinetic Resolution of Oxanorbornenes by Ring-Opening Metathesis Polymerization with a Chiral Ruthenium Initiator

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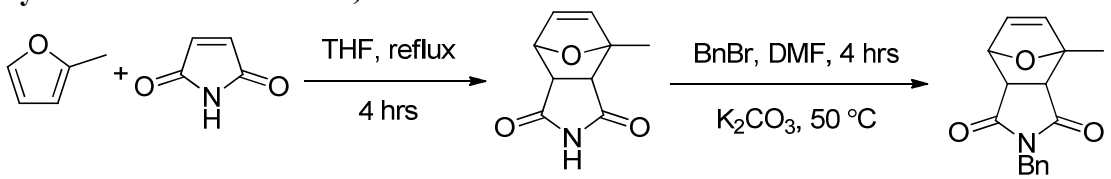
General Information

NMR spectra were recorded in $CDCl_3$ on Varian Mercury 300 MHz or INOVA 500 MHz spectrometers in the High-Resolution Nuclear Magnetic Resonance Facility at the California Institute of Technology (Caltech) operating VnmrJ software, unless otherwise noted. ^1H and ^{13}C chemical shifts are referenced relative to the residual solvent peak ($CDCl_3$ δ=7.27 for ^1H and δ=77.23 for ^{13}C). Spectral analysis was performed on MestReNova software. High-resolution mass spectra were provided by the Caltech's Mass Spectrometry Facility. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (THF) on two MZ-Gel 10 μm columns composed of styrene-divinylbenzene copolymer (Analysentechnik) and connected in series, with a miniDAWN TREOS multiangle laser light scattering (MALLS) detector, ViscoStar viscometer and Optilab rEX differential refractometer (all three from Wyatt Technologies). No calibration standards were used, as light scattering is considered an accurate measurement of molecular weight. Each sample was weighed and the dn/dc was calculated assuming 100% mass elution from the column. GPC data analysis was performed with ASTRA software. Enantiomeric excess (ee) was determined by supercritical fluid chromatography on a Chiralpak AD column from Chiral Technologies, Inc. (Daicel). The supercritical fluid is CO_2 pressurized to 100 bar. Retention times, solvents and response factors for the 210 nm UV detector for both monomers are given below.

Materials

CH_2Cl_2 was purified by passage through a solvent purification system.[1] $CDCl_3$ was obtained from Cambridge Isotopes. Initiator **I*** was prepared as reported in the manuscript, reference #. All other solvents and chemicals were obtained from Sigma-Aldrich Corporation and used as received.

Synthesis of monomer *rac, exo*-1.



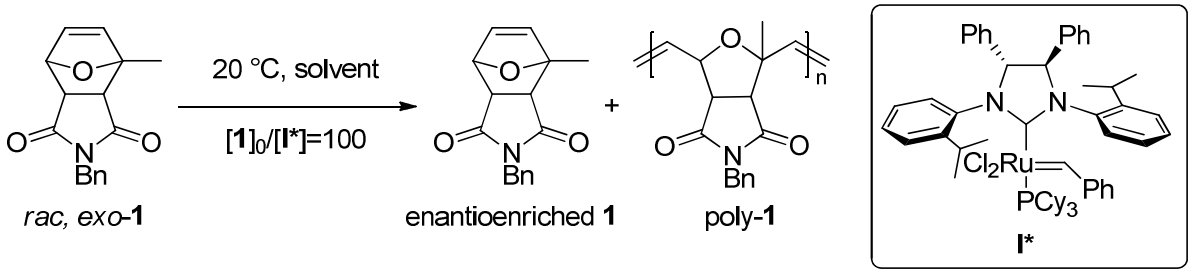
rac, exo-**1**

A 100 ml roundbottom flask equipped with a PTFE-coated stirbar was charged maleimide (1.9 g, 20 mmol, 1 equiv), 2-methylfuran (3.6 ml, 40 mmol, 2 equiv) and THF (20 ml). The flask was capped with a water-cooled reflux condenser, placed under an argon atmosphere and refluxed for 4 hours. The reaction was then cooled to room temperature. The volatiles were removed by rotary evaporation to yield a beige solid (3.39 g, 94%). The spectral characteristics of the 1-methyloxanorbornene succinimide compound match those that have been reported.[2] The compound was carried on to the next step without further purification.

In the second step, a 100 ml roundbottom flask equipped with a PTFE-coated stirbar was charged with the 1-methyloxanorbornene (1.8 g, 10 mmol, 1 equiv), K_2CO_3 (2.9, 21 mmol, 2.1 equiv) and DMF (20 ml, not dry or degassed). To this suspension was added benzyl bromide (1.3 ml, 11 mmol, 1.1 equiv.) The roundbottom flask was topped with a Vigreux column and put under argon atmosphere. The suspension was heated to 50 °C for 4 hours. The color of the solution becomes dark pink over the course of the reaction. At the end of the reaction , the solution is cooled and diluted in distilled water (100 ml). The aqueous solution was extracted with ether (3x 100ml). The combined organic layers were washed with 50% saturated aqueous

NaCl (2x 100 ml) then dried over the $MgSO_4$. The drying agent was filtered away and the volatiles were removed by rotary evaporation. The crude solid product was purified by silica gel chromatography (hexanes/ethyl acetate v/v=3) to yield *rac*, *exo*-**1** (1.44 g, 6.3 mmol, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.24 (5H, m), 6.51 (1H, dd, *J* = 6 Hz, 2 Hz), 6.33 (1H, d, *J* = 6 Hz), 5.22 (1H, d, *J* = 2 Hz), 4.66 (2H, s), 2.99 (1H, d, *J* = 6 Hz), 2.73 (1H, d, *J* = 6 Hz), 1.72 (3H, s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 175.87, 174.66, 140.61, 136.92, 135.54, 128.61, 128.03, 127.71, 127.69, 88.23, 80.67, 76.80, 50.68, 49.49, 42.38, 15.66.

Polymerization of 1.



The polymerization of *rac, exo*-**1** was conducted in a nitrogen-filled glovebox. A scintillation vial was charged with monomer **1** (269 mg, 1 mmol, 1 equiv), *p*-methoxyanisole (27 mg, 0.2 mmol, 0.2 equiv) as an internal standard and the appropriate solvent (1 ml). In another vial, chiral initiator **I*** (10 mg, 0.01 mmol, $[\mathbf{1}]_0/[\mathbf{I^*}]=100$) was dissolved in the same solvent (1 ml). The initiator solution was injected rapidly into the monomer solution. Aliquots were taken at the designated time points and the polymerization was quenched with butyl vinyl ether (0.1 ml). The series of quenched aliquots was removed from the glovebox. Each quenched aliquot was precipitated into methanol (10 ml) in a scintillation vial. The polymer suspensions were carefully filtered through folded filter paper in a funnel into a second scintillation vial. The filtered methanol solution contained enantioenriched **1**, the internal standard, and ruthenium residue. The ratio of enantiomers and conversion were determined by analysis of this solution by SFC (10% isopropanol/CO_2; depleted enantiomer=5.27 minutes and enriched enantiomer=5.66 minutes). The polymer was recovered by elution with dichloromethane from the filter paper into a third, tared scintillation vial. The volatiles were removed first by rotary evaporation then *in vacuo* overnight to yield a polymer film in most cases. The polymers were then redissolved in HPLC-grade THF and their molecular weight data was determined by GPC.

The response factor for the *p*-methoxyanisole internal standard compared to *rac,exo*-**1** at 210 nm is the ratio of the slopes of their concentration curves: 712500/356600=2. The same standard solutions measured two months later only changed slightly (<1%).

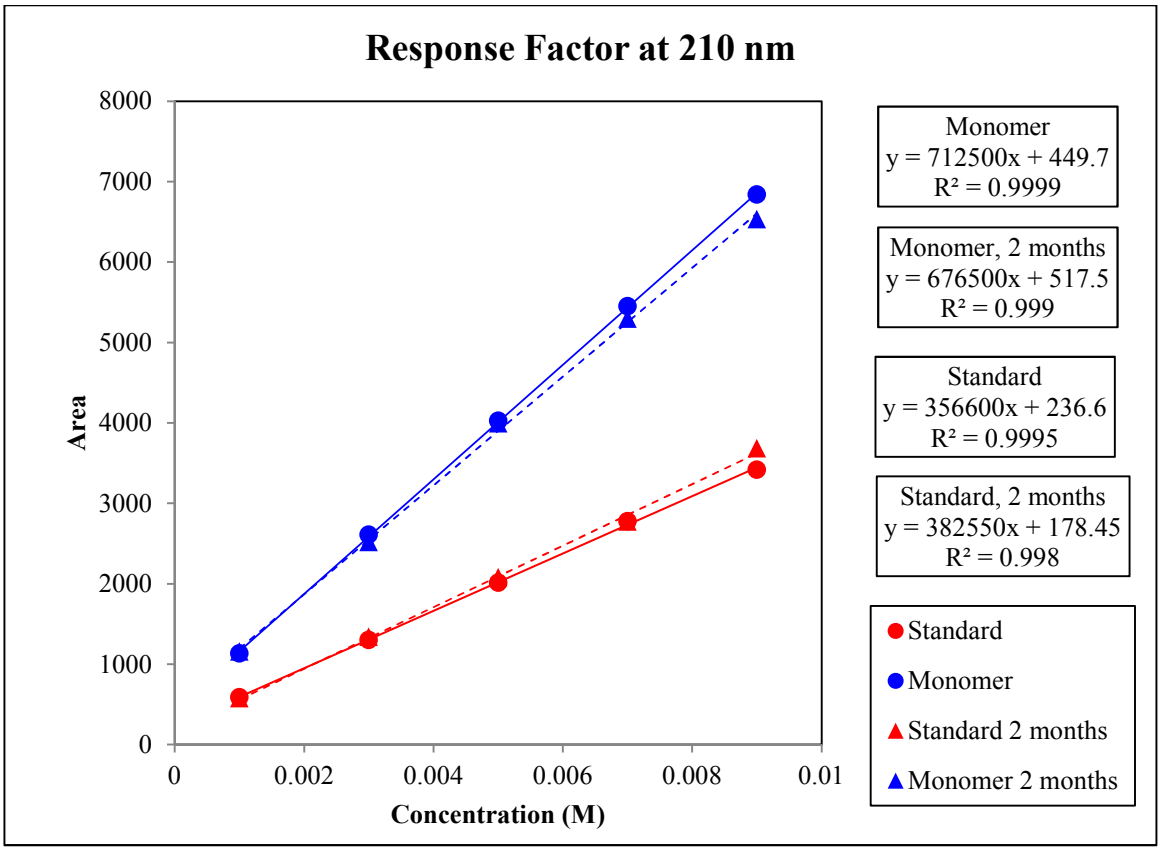
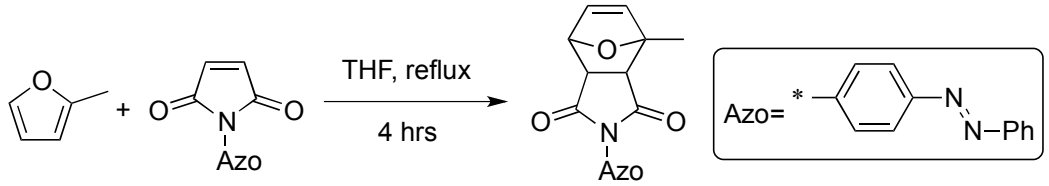

Response Factor at 210 nm
Area
Concentration (M)
0
1000
2000
3000
4000
5000
6000
7000
8000
0
0.002
0.004
0.006
0.008
0.01
Monomer
y = 712500x + 449.7
R² = 0.9999
Monomer, 2 months
y = 676500x + 517.5
R² = 0.999
Standard
y = 356600x + 236.6
R² = 0.9995
Standard, 2 months
y = 382550x + 178.45
R² = 0.998
Standard
Monomer
Standard 2 months
Monomer 2 months

Table 1. Polymerization Kinetics

Solvent	Time (min)	Conversion (%)[a]	*ee* (%)[a]	*S*[a]	M_w (Da)	PDI	M_n (Da)	M_n, theor. (Da)
THF	6	20	7	1.9	30080	1.104	27250	5408
THF	10	28	15	2.6	38600	1.205	32030	7642
THF	16	40	29	3.3	50140	1.169	42900	10795
THF	20	46	39	3.8	55290	1.202	46010	12378
DCM	10	15	5	1.9	13850	1.231	11250	4011
DCM	15	23	10	2.1	24830	1.239	20040	6292
DCM	20	33	15	2.2	32850	1.236	26570	8880
DCM	25	34	22	3.0	47850	1.217	39410	9183
PhMe	10	5	5	16	38390	1.370	27480	1480
PhMe	20	19	12	3.6	57980	1.264	45850	5074
PhMe	30	36	24	3.1	74580	1.281	58240	9653
PhMe	40	48	35	3.0	83700	1.343	62300	13009
PhMe	4	7	7	20				
PhMe	13	15	9	3.5				
PhMe	24	22	13	3.1				

(a) The selectivity was calculated assuming first order monomer consumption, using the equation S=ln[(1-c)(1-ee)]/ln[(1-c)(1+ee)]. This approximation is used because the actual kinetics of this resolution are challenging to analyze due to the changing chiral control elements.

Synthesis of monomer *rac, exo*-2.

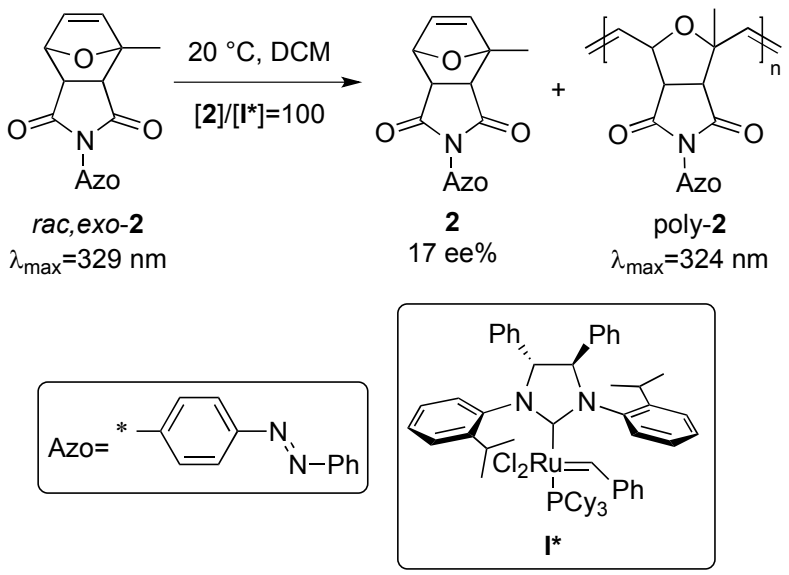


rac,exo-**2**

λ_{max}=329 nm

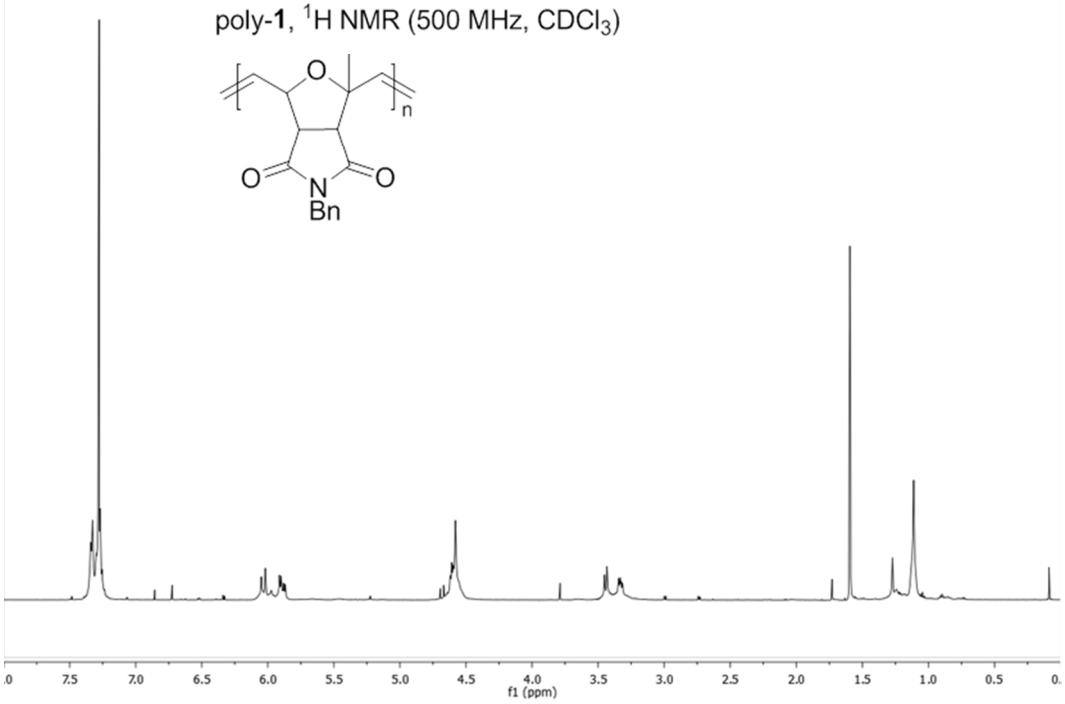
A 2-dram vial equipped with a PTFE-coated stirbar was charged with 4-phenylazomaleinanil (277 mg, 1 mmol, 1 equiv), THF (1 ml), and 2-methylfuran (180 µl, 2 mmol, 2 equiv). The 4-phenylazomaleinanil was insoluble at room temperature, but dissolved upon heating. The reaction mixture was heated to 65 °C for 4 hours, then allowed to slowly cool to room temperature. The product precipitated from solution as an orange powder. The orange solid was filtered then dried overnight *in vacuo* to yield *rac, exo*-**2** (184 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (2H, m), 7.93 (2H, dd, J = 8 Hz, 2 Hz), 7.57–7.45 (5H, m), 6.58 (1H, dd, J = 6 Hz, 2 Hz), 6.39 (1H, d, J = 6 Hz), 5.34 (1H, d, J = 2 Hz), 3.17 (1H, d, J = 6 Hz), 2.90 (1H, d, J = 6 Hz), 1.82 (3H, s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 175.07, 173.81, 152.54, 151.96, 140.80, 137.12, 131.33, 129.12, 127.12, 123.45, 123.01, 88.73, 81.21, 76.76, 50.73, 49.59, 15.78.

Polymerization of *rac, exo*-2.

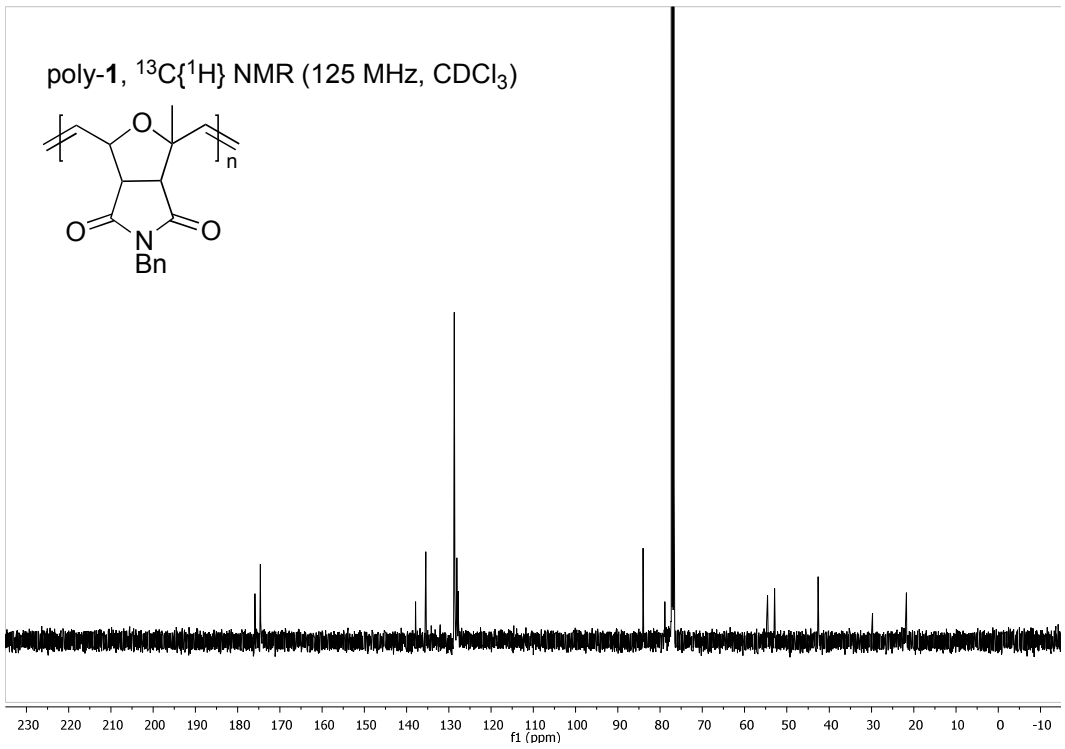


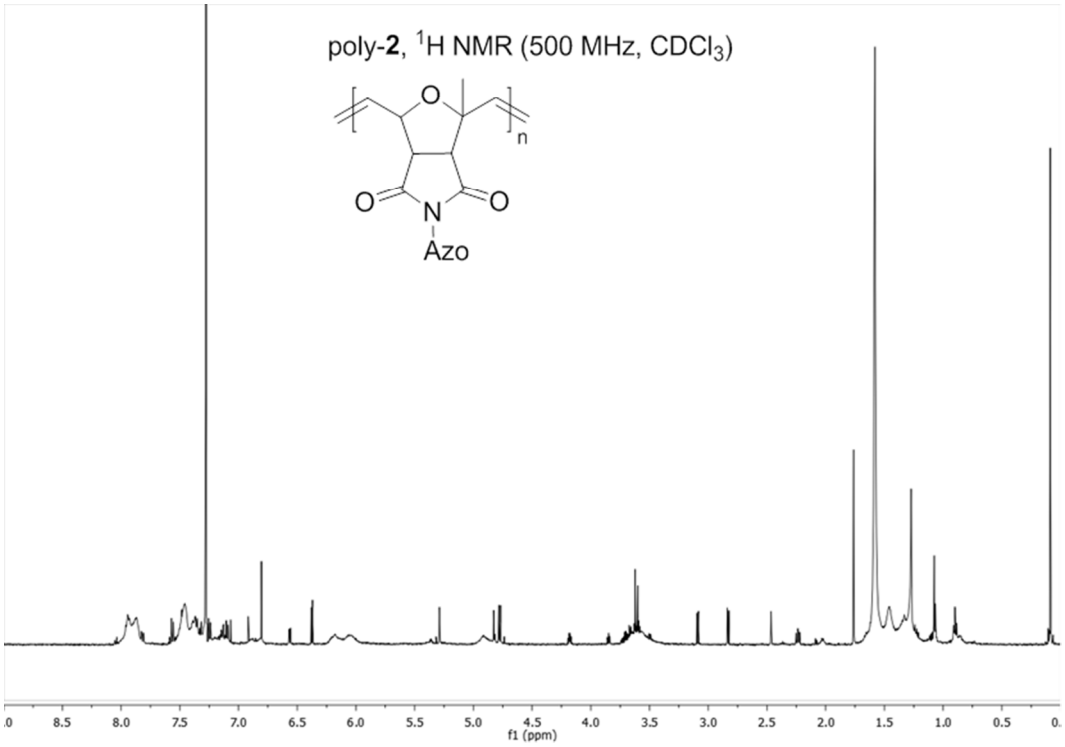
In a nitrogen-filled glovebox, a vial was charged with **2** (90 mg, 0.25 mmol) and dichloromethane (0.5 ml). In a separate vial, initiator **I*** (2.5 mg, 2.5 μmol, $[\mathbf{2}]_0/[\mathbf{I^*}]=100$) was dissolved in dichloromethane (0.5 ml). The initiator solution was added in one portion to the monomer solution. The reaction vial was sealed and removed from the glovebox. The polymerization was allowed to react for 40 minutes and was quenched with ethyl vinyl ether (100 μl) for 5 minutes. The reaction mixture was precipitated into methanol (10 ml) in a scintillation vial. The polymer suspensions were carefully filtered through folded filter paper in a funnel into a second scintillation vial. The filtered methanol solution contained enantioenriched **2** and ruthenium residue. The ratio of enantiomers was determined by analysis of this solution by SFC (20% isopropanol; depleted enantiomer=8.83 minutes and enriched enantiomer=8.44 minutes). The polymer was recovered by elution with dichloromethane from the filter paper into a third, pre-weighed scintillation vial. The volatiles were removed first by rotary evaporation then *in vacuo* overnight to yield a polymer film (10 mg).

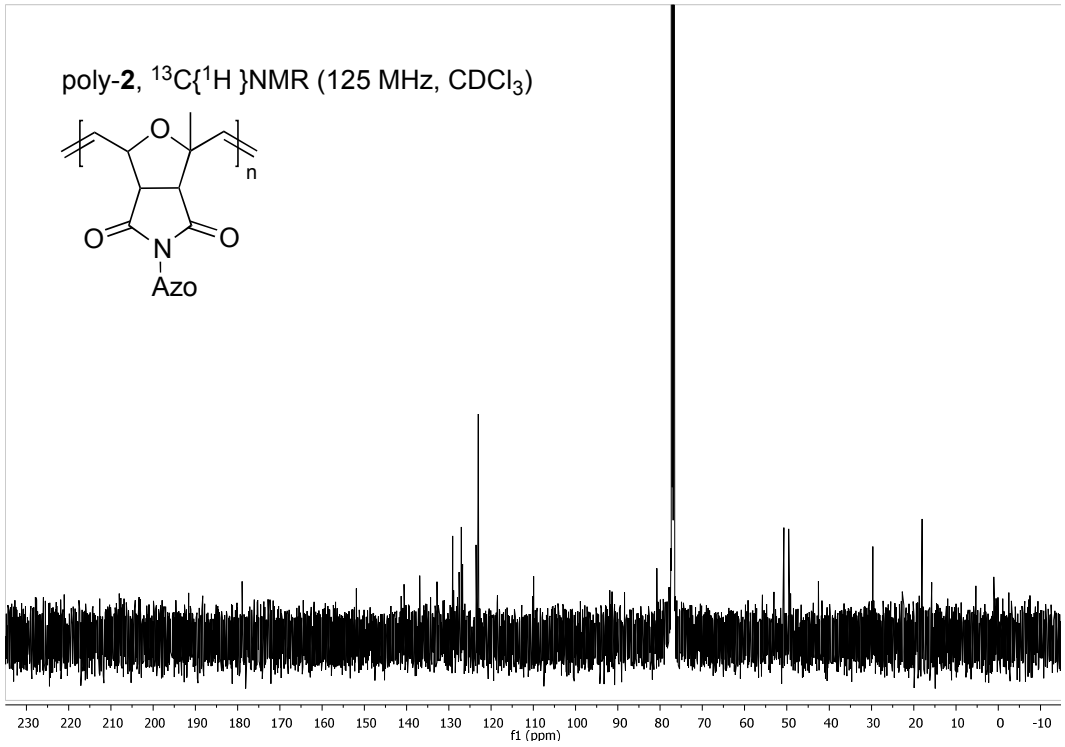
poly-**1**, ^{1}H NMR (500 MHz, $CDCl_3$)

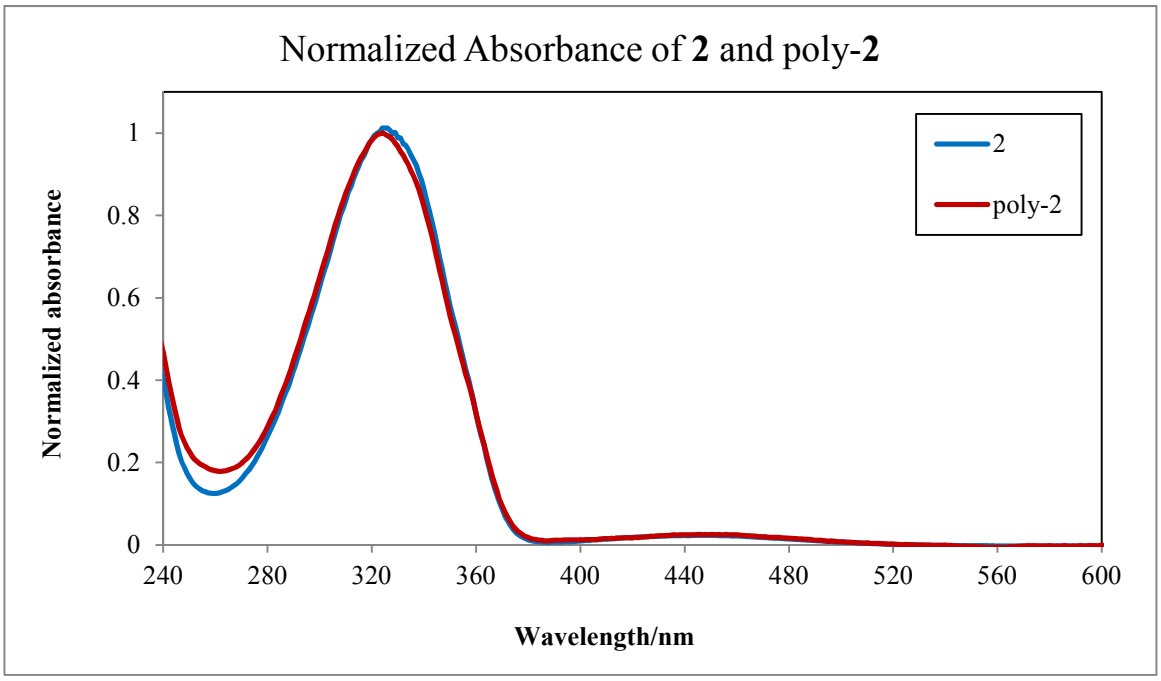


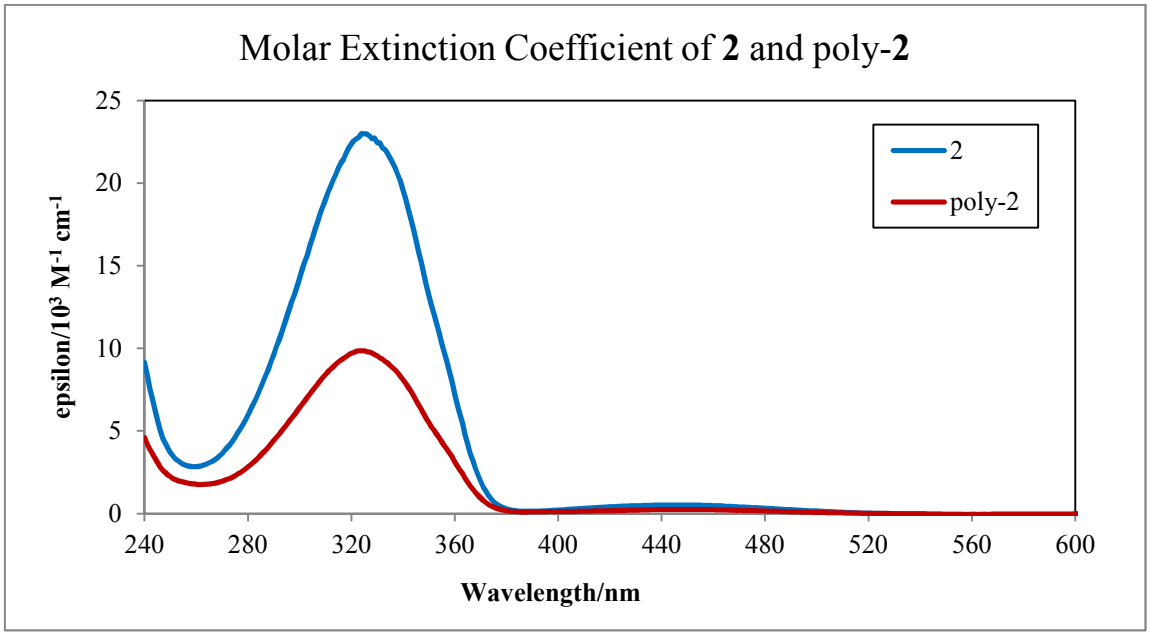
poly-**1**, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)




poly-2, ^{1}H NMR (500 MHz, $CDCl_3$)
O
n
O
N
O
Azo
f1 (ppm)


poly-2, $^{13}C\{^{1}H\}$NMR (125 MHz, $CDCl_3$)
O
n
O
N
O
Azo
f1 (ppm)





[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
[2] Lu, Z.; Weber, R.; Twieg, R. J. *Tetrahedron Lett.* **2006**, *47*, 7213-7217.