Supporting Information

Ruthenium Catalyzed Equilibrium Ring-Opening Metathesis Polymerization of Cyclopentene

Robert Tuba,[1]* Robert H. Grubbs[1,2]*

[1]Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar. [2]The Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States.

*Email: rhg@caltech.edu; robert.tuba@tamu.edu.

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General information

All reactions were conducted under Argon atmosphere. Ruthenium catalysts **1** and **2** (Materia), cyclopentene (Aldrich), ethyl vinyl ether (Aldrich), norbornene (Aldrich) toluene-d_8 (Cambridge Isotope or Aldrich) and other solvents, were used as received. Catalyst **3** was synthetized following literature procedures.[1]

NMR experiments were performed at 25 ^{o}C. All NMR samples were stabilized at 25 °C for 5 min before data collection. All the screw capped, gas tight NMR tubes were flame dried and evacuated *in vacuo* in advance. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer in Toluene-d_8 and referenced to residual internal toluene (δ = 2.09 ppm ^{1}H and 20.4 ppm ^{13}C). The quantitative ^{13}C NMR spectra for *cis*/*trans* bond ratio determination were recorded with inverse gated decoupling at 10 s relaxation delay.

GPC analyses were carried out using a Viscotek GPC Max VE 2001 instrument with a Viscotek TDA 302 triple array detector and Viscotek Org Guard column with three (in series) Mixed Medium columns (LT5000L) at 35 °C and a flow rate of 1.0 mL/min. A 12-point Universal Calibration Standard calibration curve was recorded. From each sample three measurements have been carried out and the averages have been reported. A during the tests a second calibration curve has been recorded with polystyrene (PS) standards and the measured MW values of the samples were corrected with the multiplication of the measured values with 0.938.

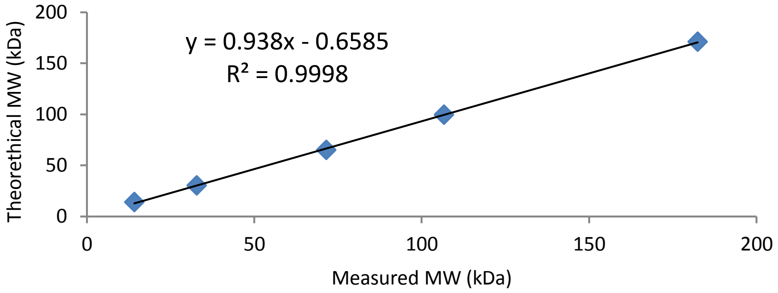

Figure S1. GPC calibration with PS standards, theorethical vs measured MW values (kDa).

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[1] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics*, **2001**, *20*, 5314.

Investigation of the impact of reaction temperature on the ROMP of cyclopentene.

All the experiments were performed under the same conditions including vessel type, stirrer shape and size and concentration ranges at 0, 10, 20 and 30 °C. In a glove box, 10 mL, oven-dried round bottom flasks were charged with 4.2 mg (0.00495 mmol) **2** catalyst and 0.8 mL freshly opened toluene-d_8. The vessels were sealed with gas tight septa, taken out of the glovebox and cooled down to the target temperature under continuous stirring (500 rpm). Then 0.20 mL (2.17 mmol) cyclopentene was added by a 1.0 mL Hamilton glass syringe under inert atmosphere. After two hours, the reaction mixtures were quenched with 0.10 mL (1.044 mmol) ethyl vinyl ether. The solutions were stirred for an additional 15 minutes then 0.5 mL samples were transferred into sealable NMR tubes. ^{1}H NMR spectra were recorded for each sample and the conversion was determined by the ratio of the integrals of the peaks at 5.70 ppm (cyclopentene, CH, s) and 5.45 ppm (polypentenamer, CH, br, s), ethyl vinyl ether was used as internal standard. The *cis*/*trans* ratio of the bonds was determined by quantitative ^{13}C NMR spectra recorded in toluene-d_8 following the evaporation of the volatiles from the rest of the mixture remained in the reaction vessel. The *cis*/*trans* ratio was determined according to the integral of the peaks at 130.7 and 130.1 ppm. The solvents were then evaporated from the sample and the remaining rubber like residues were dissolved in THF to obtain 1.0 mg/mL polymer solution for GPC test (Figure S2-S6).

Thermodynamic data calculation. (See also Table 1. and Figure 1.) According to the equilibrium polymerization theory the thermodynamic data were calculated from the following relationships:

$$\boldsymbol{ln}[\boldsymbol{M}] = \frac{\Delta H}{R * T} - \frac{\Delta S}{R} \tag{1}$$

where [M] is the monomer equilibrium concentration, *ΔH* is the activation enthalpy (kJ mol^{-1}) during the polymerization, R is the universal gas constant (8.3144 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature in degrees Kelvin (K) and *ΔS* is the activation entropy ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). *ΔH* can be calculated from the slope of the line in Figure 1. ($m = -2.80 \cdot 10^3$ K) according to the following equation (1 kcal = 4.184 kJ):

$$\Delta \boldsymbol{H} = m \cdot R \tag{2}$$

$$\Delta \boldsymbol{H} = -2.80 \cdot 10^3 K \cdot 8.31\, J \cdot mol^{-1} \cdot K^{-1} = \boldsymbol{-23.28\, kJ \cdot mol^{-1}}$$

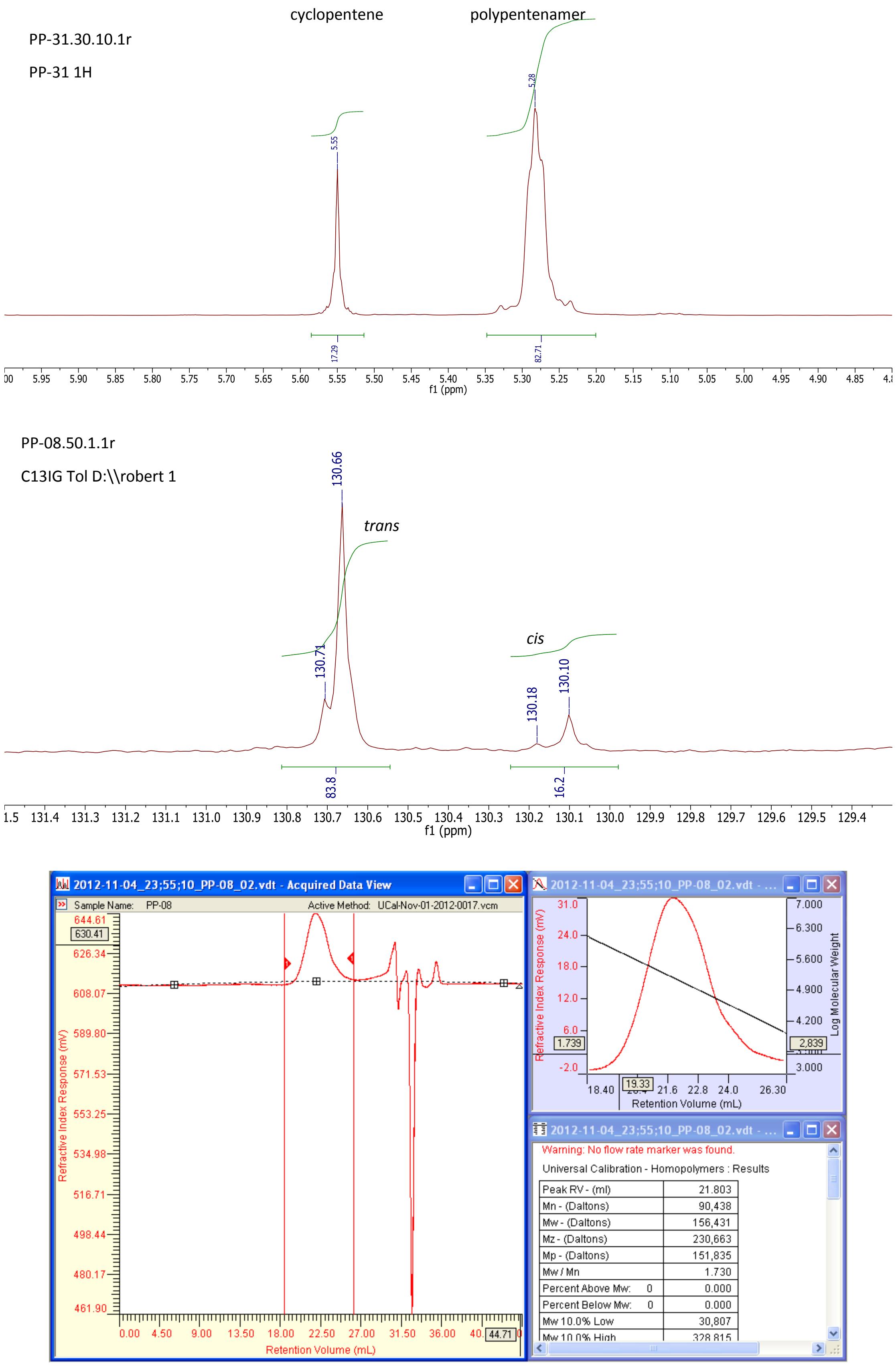
$$\Delta \boldsymbol{H} = \boldsymbol{-5.56\, kcal \cdot mol^{-1}}$$

The standard entropy change can be calculated with the rearrangement of equation (1):

$$\Delta S = \frac{\Delta H}{T} - R \cdot \ln[M] \tag{3}$$

$$\Delta S = \frac{-23268\, J \cdot\ mol^{-1}}{273\, K} - 8.31 \cdot \ln[0.385] = \boldsymbol{-77.30\, J \cdot mol^{-1} \cdot K^{-1}}$$

$$\Delta \boldsymbol{S} = \boldsymbol{-18.47\, cal \cdot mol^{-1}\ \cdot K^{-1}}$$



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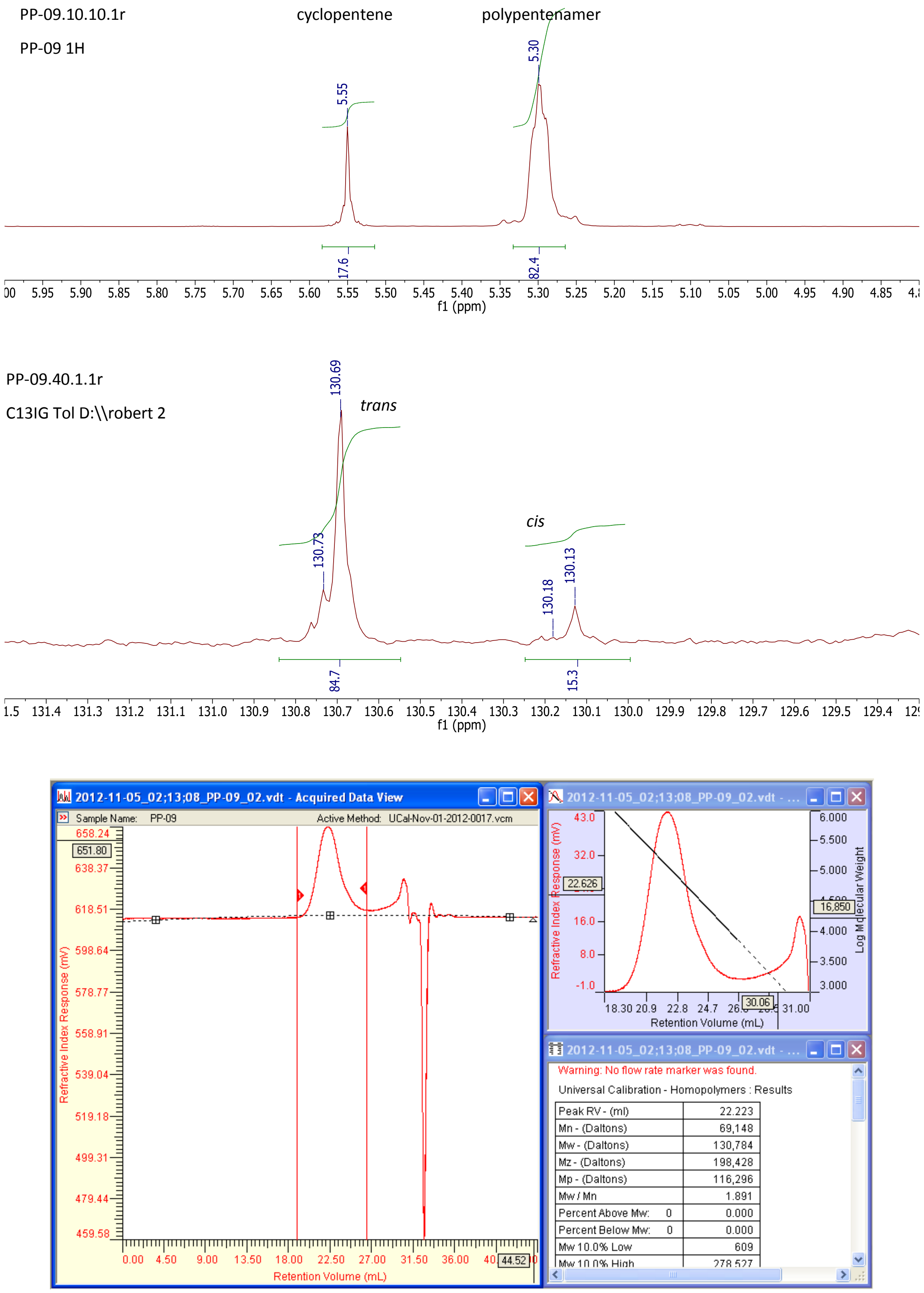
Universal Calibration - Homopolymers : Results

Peak RV - (ml)	21.803
Mn - (Daltons)	90,438
Mw - (Daltons)	156,431
Mz - (Daltons)	230,663
Mp - (Daltons)	151,835
Mw / Mn	1.730
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	30,807
Mw 10.0% High	328,815

Figure S2. ^{1}H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-d_8 at 0 °C. Quantitative ^{13}C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.



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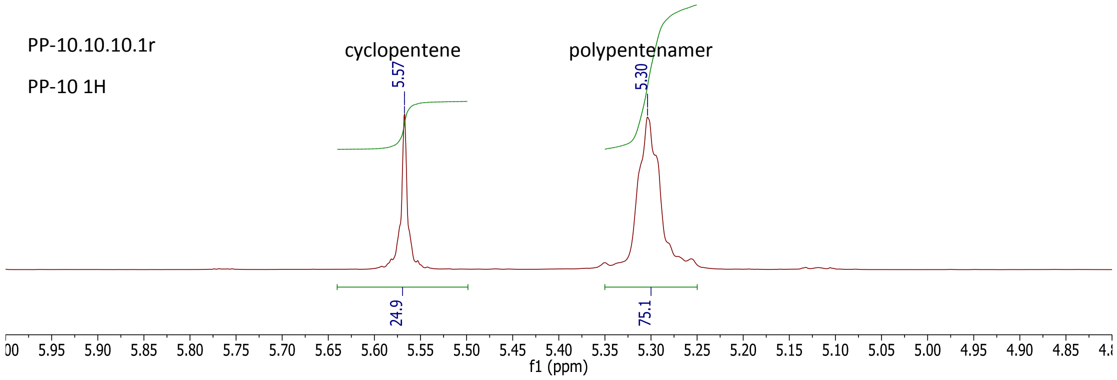
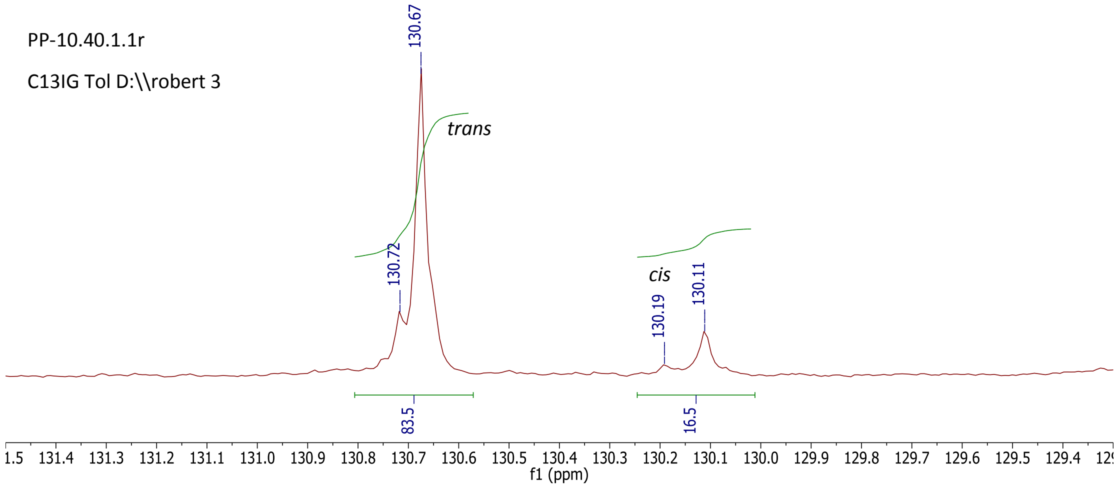
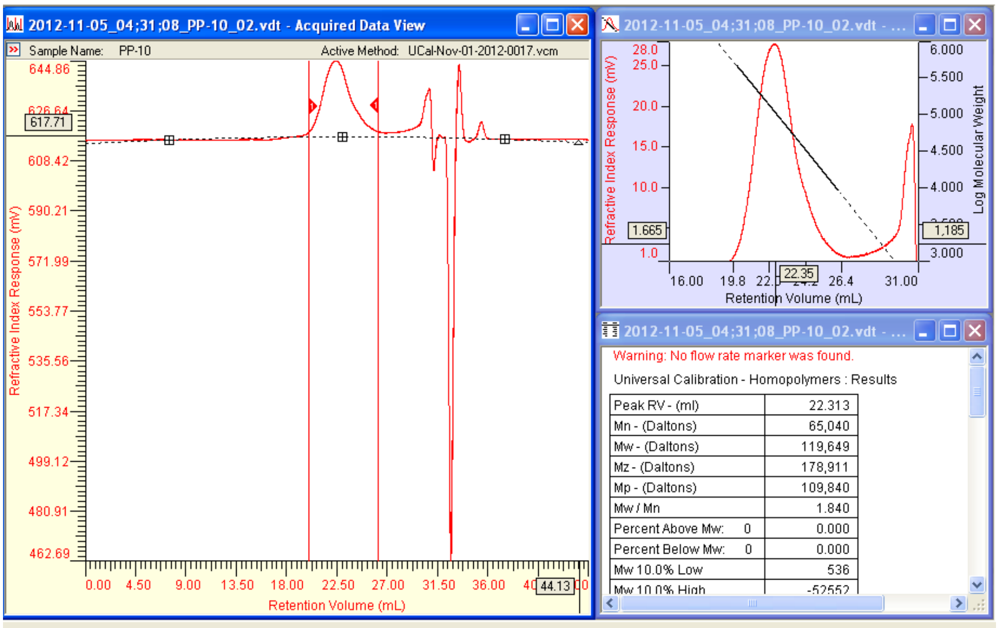
Universal Calibration - Homopolymers : Results

Peak RV - (ml)	22.223
Mn - (Daltons)	69,148
Mw - (Daltons)	130,784
Mz - (Daltons)	198,428
Mp - (Daltons)	116,296
Mw / Mn	1.891
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	609
Mw 10.0% High	278,527

Figure S3. ^{1}H NMR spectrum (top) of the reaction mixture quenched at 5 hour in toluene-d_8 at 0 °C. Quantitative ^{13}C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.







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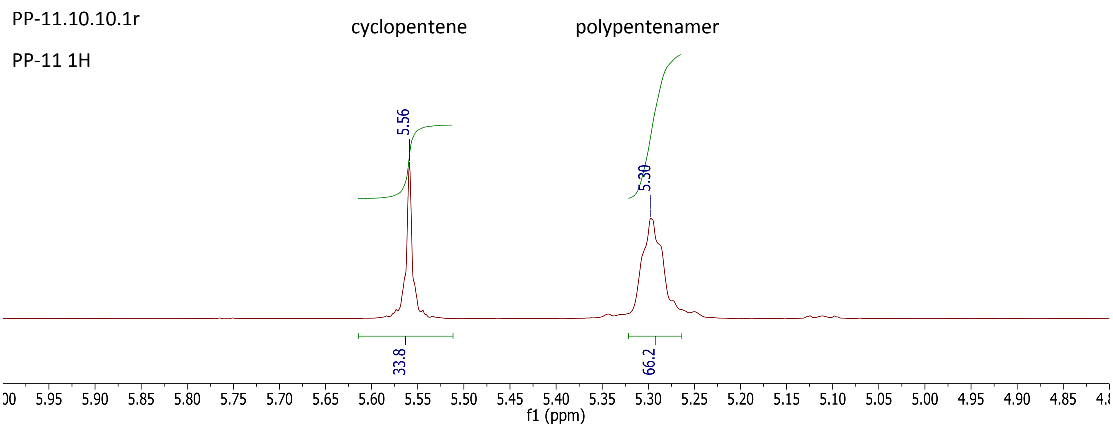
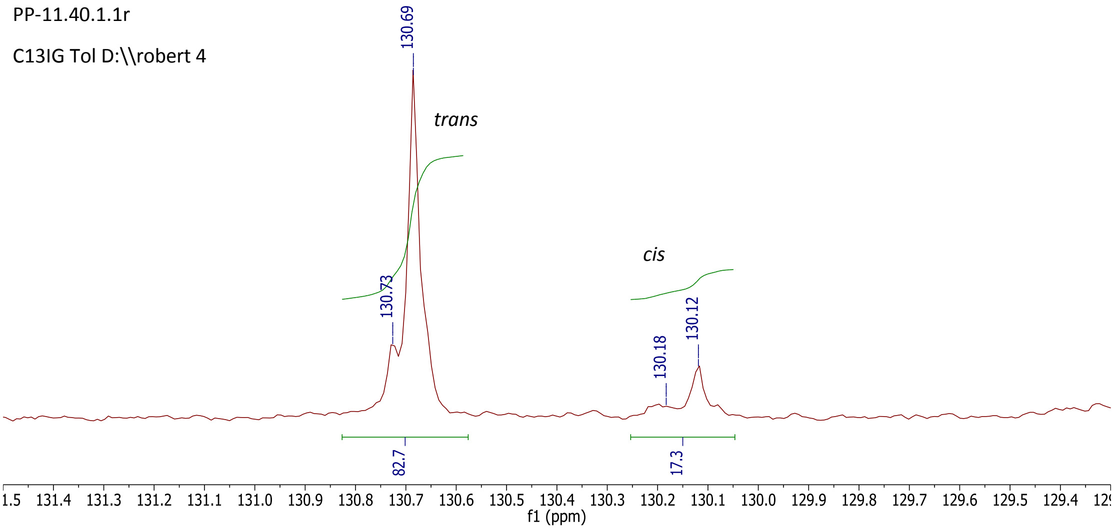
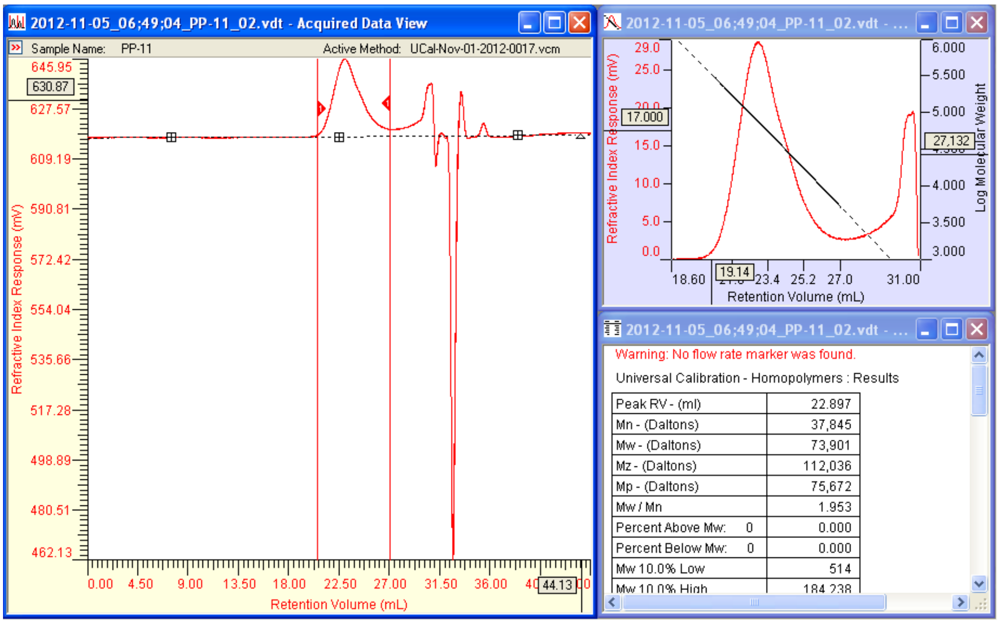
Universal Calibration - Homopolymers : Results

Peak RV - (ml)	22.313
Mn - (Daltons)	65,040
Mw - (Daltons)	119,649
Mz - (Daltons)	178,911
Mp - (Daltons)	109,840
Mw / Mn	1.840
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	536
Mw 10.0% High	-52552

Figure S4. ^{1}H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-d_8 at 10 °C. Quantitative ^{13}C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.







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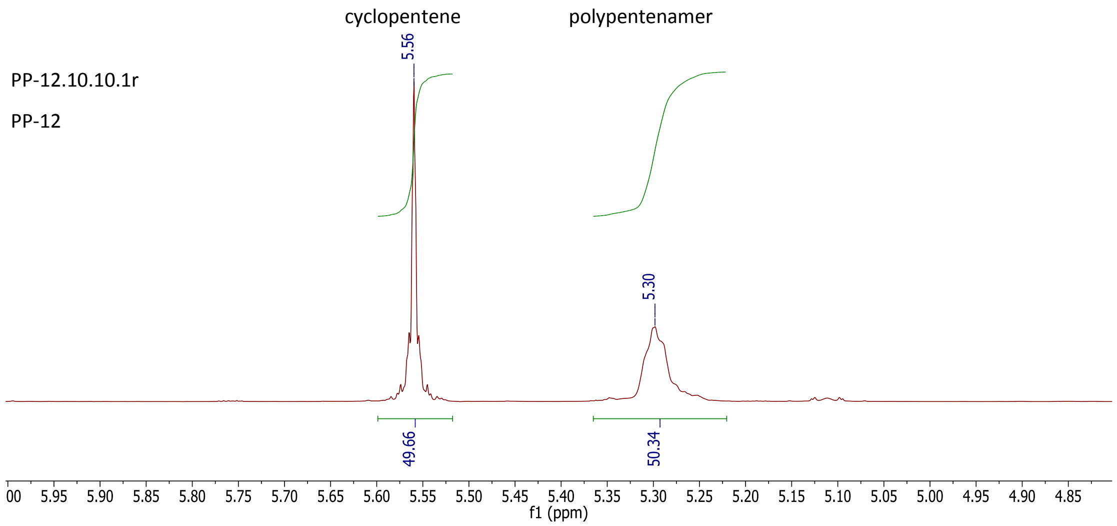
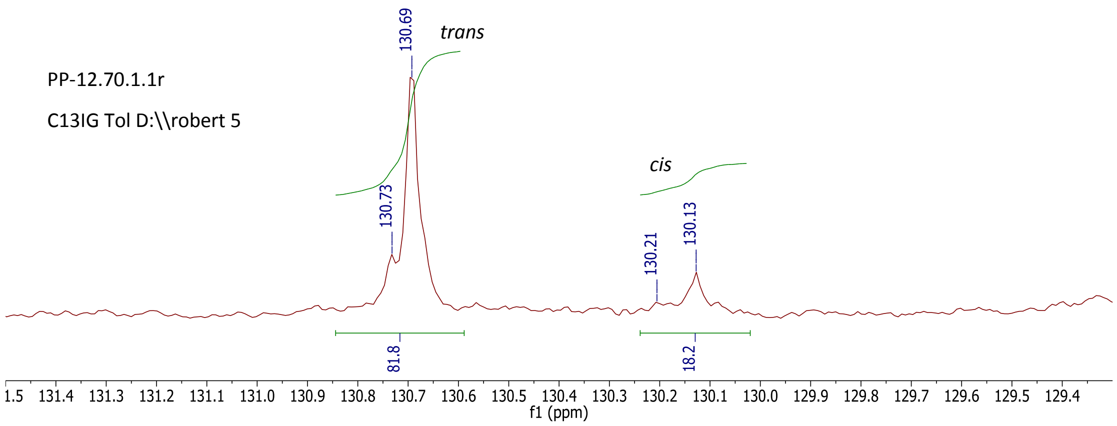
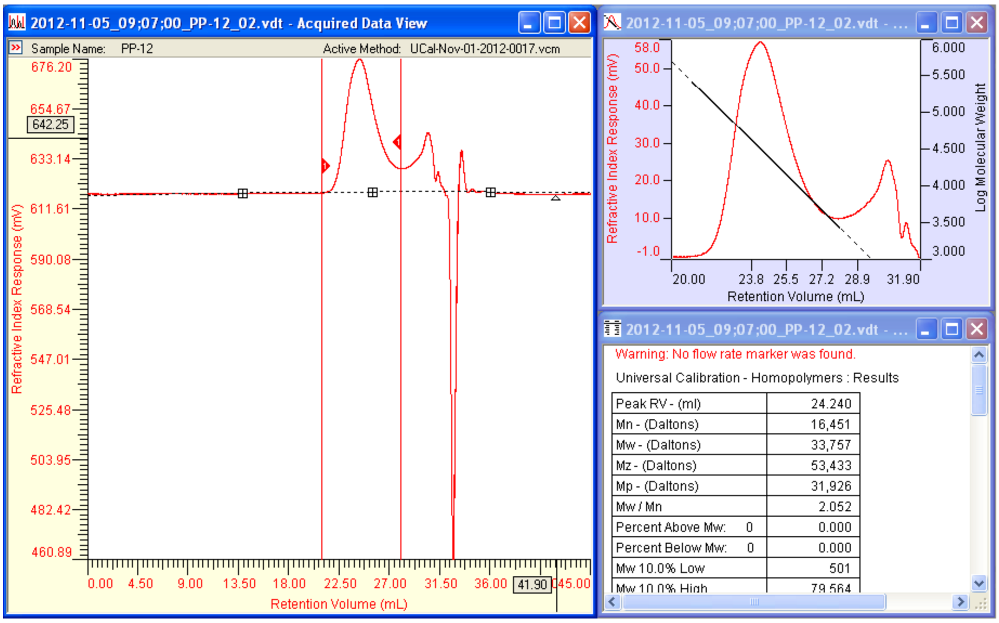
Universal Calibration - Homopolymers : Results

Peak RV - (ml)	22.897
Mn - (Daltons)	37,845
Mw - (Daltons)	73,901
Mz - (Daltons)	112,036
Mp - (Daltons)	75,672
Mw / Mn	1.953
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	514
Mw 10.0% High	184,238

Figure S5. ^{1}H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-d_8 at 20 °C. Quantitative ^{13}C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.







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Universal Calibration - Homopolymers : Results

Peak RV - (ml)	24.240
Mn - (Daltons)	16,451
Mw - (Daltons)	33,757
Mz - (Daltons)	53,433
Mp - (Daltons)	31,926
Mw / Mn	2.052
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	501
Mw 10.0% High	79,564

Figure S6. ^{1}H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-d_8 at 30 °C. Quantitative ^{13}C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.

Investigation of the impact of catalyst loading on the ROMP of cyclopentene.

All the experiments were performed in the same conditions including vessel type, stirrer shape and size at 0 °C. In the glove box a 10 mL, oven-dried round bottom flasks were charged with 2.2 mg (0.00259 mmol), 4.2 mg (0.00495 mmol), 10.3 mg (0.01213 mmol), 20.5 mg (0.02415 mmol) catalyst **2** and 0.8 mL freshly opened toluene-d_8. The vessels were sealed with gas tight septa, taken out of the glovebox and cooled down to 0 °C under continuous stirring (500 rpm). Then 0.20 mL (2.17 mmol) cyclopentene was added by a 1.0 mL Hamilton glass syringe under inert atmosphere. After two hours the reaction mixtures were quenched with 0.10 mL (1.044 mmol) ethyl vinyl ether. The solutions were stirred for additional 15 minutes then 0.5 mL samples were transferred into a sealable NMR tubes. ^{1}H NMR spectra were recorded for each sample and the conversion was determined by the ratio of the integrals of the peaks at 5.70 ppm (cyclopentene, CH, s) and 5.45 ppm (polypentenamer, CH, br, s), ethyl vinyl ether was used as internal standard. Then the volatiles were evaporated from the rest of the mixture remained in the reaction vessel. The remaining rubber like residues was dissolved in THF to obtain 1.0 mg/mL polymer solution for GPC test.

Table S1. Cyclopentene conversion at different catalyst loading. Toluene-d_8 solution; [M] = 2.17 M; catalyst: **2**; t = 0 °C.

Entry	[**2**] (mM)	t_r (h)	Conversion (%)	$MW_{theorethical}$ (kDa)	$MW_{theorethical}$ Corrected with conversion (kDa)	$MW_{measured}$ (kDa)	PDI
1	2.59	2	34.5	59.44	20.51	98.8	1.815
2	4.89	2	82.2	31.48	25.12	145.4	1.757
3	5.06	5	82.4	30.43	25.07	122.3	1.877
4	12.13	2	83.7	12.69	10.62	156.7	1.702
5	24.15	2	83.6	6.37	5.33	76.3	1.959

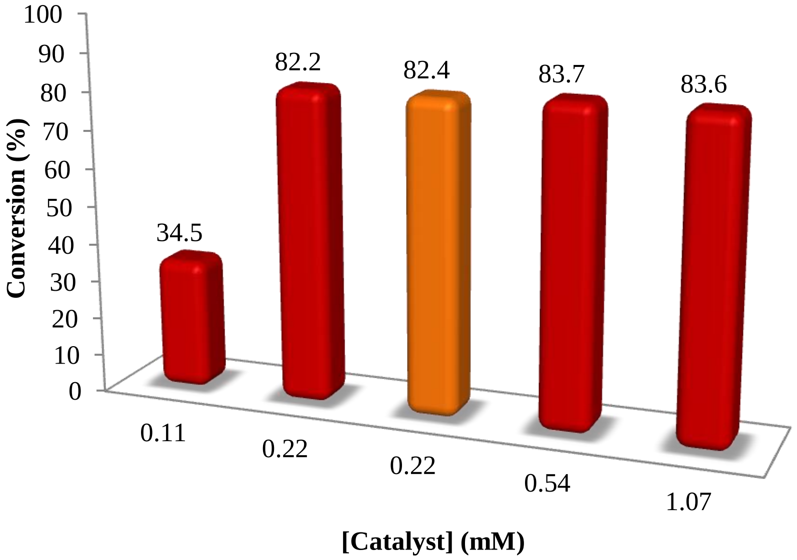

Figure S7. Cyclopentene conversions obtained at different catalyst **2** loading. Toluene-d_8 solution; [cyclopentene] = 2.17 M; catalyst **2**; t = 0 °C; t_r = 2h (red), 5h (orange).

Investigation of the impact of different Ru catalyst systems on the ROMP of cyclopentene.

All the experiments were performed in the same conditions including vessel type, stirrer shape and size at 0 °C. In a glove box, a 10 mL, oven-dried round bottom flasks were charged with 2.0 mg (**1**, 0.00486 mmol), 2.2 mg (**2**, 0.00259 mmol) and 4.4 mg (**3**, 0.00497 mmol) catalysts and 0.8 mL freshly opened toluene-d_8. The vessels were sealed with gas tight septa, taken out of the glovebox and cooled down to 0 °C under continuous stirring (500 rpm). Then 0.20 mL (2.17 mmol) cyclopentene was added by a 1.0 mL Hamilton glass syringe under inert atmosphere. After two hours the reaction mixtures were quenched with 0.10 mL (1.044 mmol) ethyl vinyl ether. The solutions were stirred for additional 15 minutes then 0.5 mL samples were transferred into sealable NMR tubes. ^{1}H NMR spectra were recorded for each sample and the conversion was determined by the ratio of the integrals of the peaks at 5.70 ppm (cyclopentene, CH, s) and 5.45 ppm (polypentenamer, CH, br, s), ethyl vinyl ether was used as internal standard. Then the volatiles were evaporated from the rest of the mixture remained in the reaction vessel. The remaining rubber like residues was dissolved in THF to obtain 1.0 mg/mL polymer solution for GPC test.

Table S2. Cyclopentene conversion with different catalyst systems. Toluene-d_8 solution; [M] = 2.17 M; t = 0 °C; t_r = 2h, (entry 3: t_r = 5h).

Entry	Catalyst	[Catalyst] (mM)	Conversion (%)	$MW_{theorethical}$ (kDa)	$MW_{theorethical}$ Corrected with conversion (kDa)	$MW_{measured}$ (kDa)	PDI
1	1	4.86	70.2	31.68	22.24	87.8	1.703
2	2	4.89	82.2	31.48	25.12	145.4	1.757
3	2	5.06	82.4	30.43	25.07	122.3	1.877
4	3	4.97	82.3	30.98	25.49	68.6	1.885

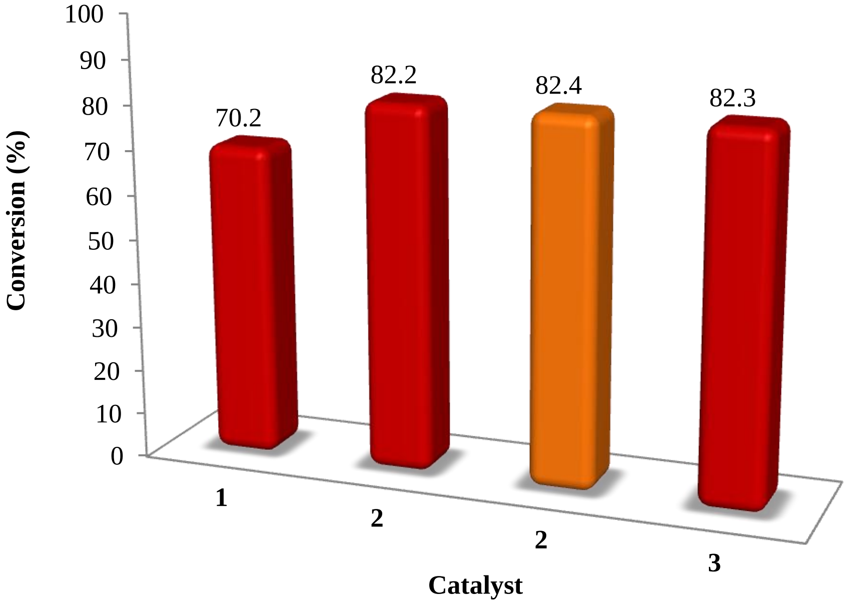

Figure S8. Cyclopentene conversion with different catalyst systems. Toluene-d_8 solution; [M] = 2.17 M; t = 0 °C; t_r = 2h (red), 5h (orange).