Optimizing Ring Strain Energy Predictions Towards Chemically Recyclable Materials.

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Introduction

When we throw away certain materials into the recycling bin rather than general waste, where exactly do those materials end up? Only 9% of the 6.3 billion metric tons of plastic produced to date has actually been recycled leaving the rest to reside in landfills, the environment, or undergo combustion.[1] One approach to addressing the plastic crisis is through chemical recycling to monomer (CRM). The goal of CRM is to create a circular polymer economy where materials can be selectively polymerized into product and depolymerized back into monomer without the loss of important material properties.[2] A promising polymerization is equilibrium Ring Opening Metathesis Polymerization (ROMP) due to its dependence on catalysts and ring strain energies (RSEs). Systems with lower RSE, like cyclopentenes, are sensitive to reaction conditions and offer a promising route towards novel materials potentially capable of CRM.[3] Through computation, we can accurately predict the RSE which can guide and expedite experimental design. RSE predictions can help analyze the efficiency at which materials can be chemically recycled as well as identify ideal reaction conditions to accomplish these feats to create sustainable and more environmentally friendly plastics.
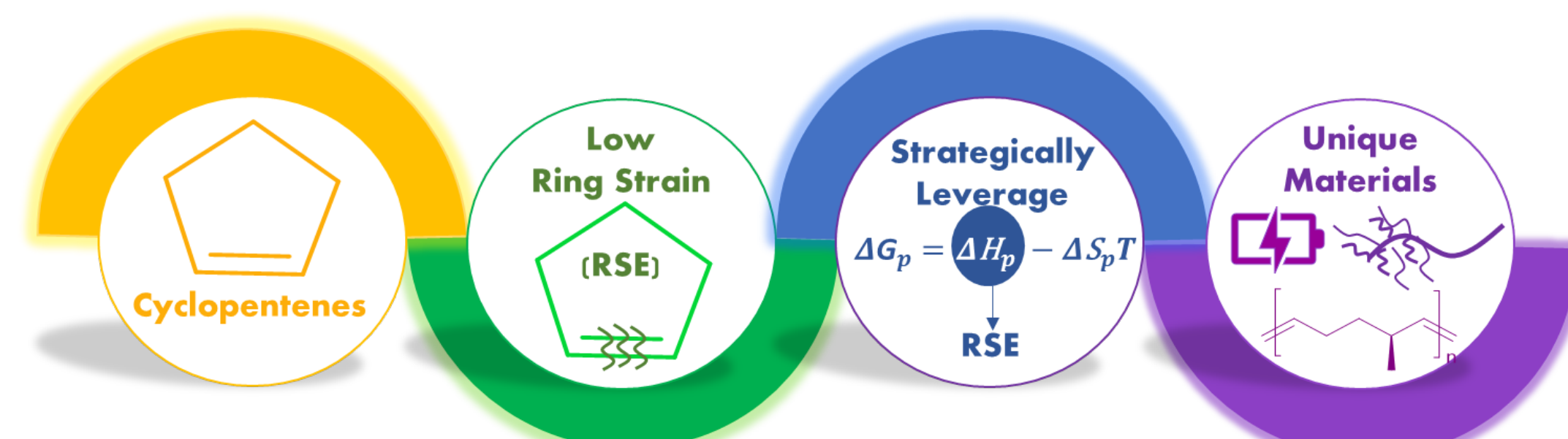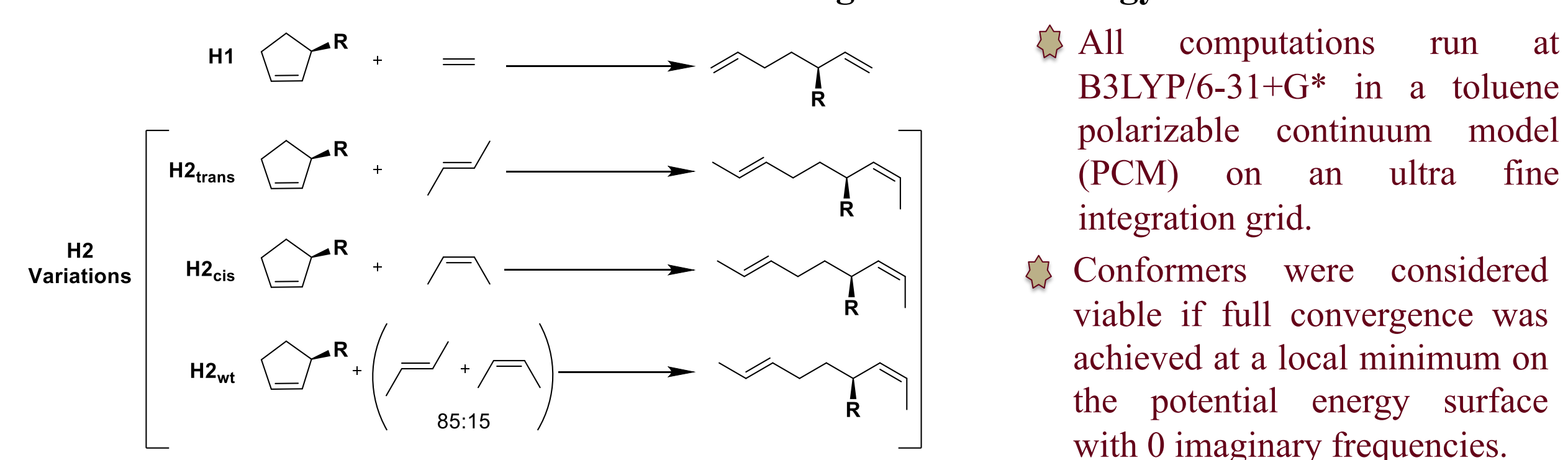

Figure 1. Benefits of understanding and accurately predicting RSE of low strain monomers, such as cyclopentenes, towards strategically exploiting metathesis events to afford novel materials.

Experimental Design

1. *Cis/Trans* conformational considerations using the lowest energy conformers:

- All computations run at B3LYP/6-31+G* in a toluene polarizable continuum model (PCM) on an ultra fine integration grid.
- Conformers were considered viable if full convergence was achieved at a local minimum on the potential energy surface with 0 imaginary frequencies.

Scheme 1. The allylic version of homodesmotic reactions used to predict the RSE of CP derivatives. **H1** is the previously reported homodesmotic reaction for RSE predictions. **H2** is the proposed homodesmotic reaction designed to consider olefin conformational changes naturally seen in ROMP. **H2_trans**, **H2_cis**, and **H2_wt** contain 1:0, 0:1, and *85:15 trans:cis* but-2-ene respectively, where **H2_wt** mimics the *85:15 trans: cis* ratio typically observed in polypentenamer backbones.
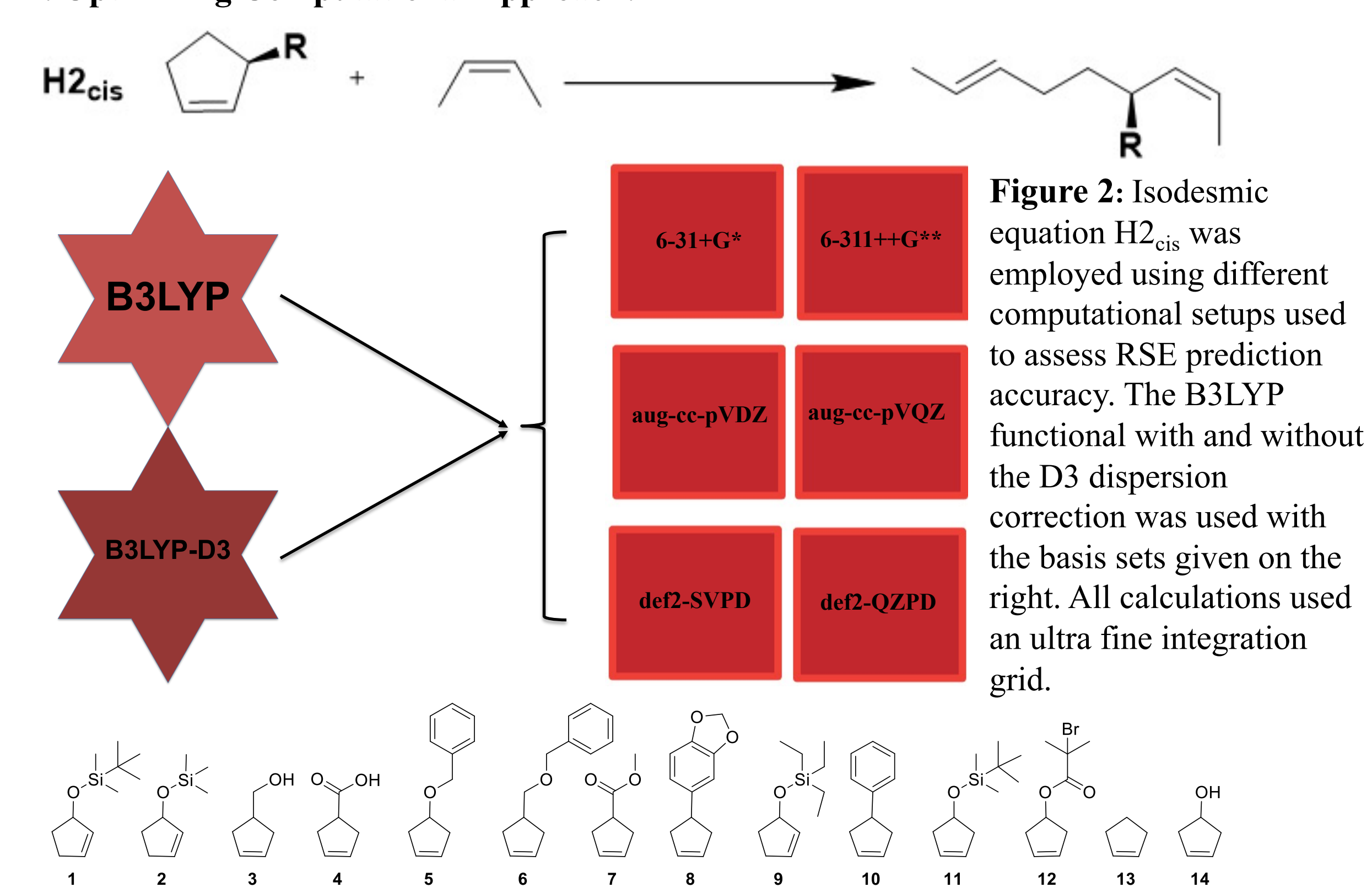
2. Optimizing Computational Approach:

Figure 2. Isodesmic equation H2_cis was employed using different computational setups used to assess RSE prediction accuracy. The B3LYP functional with and without the D3 dispersion correction was used with the basis sets given on the right. All calculations used an ultra fine integration grid.

Scheme 2: Commonly used CP Monomers with previously reported experimental ΔH_p values

Results

a. New Isodesmic Equations (H2)

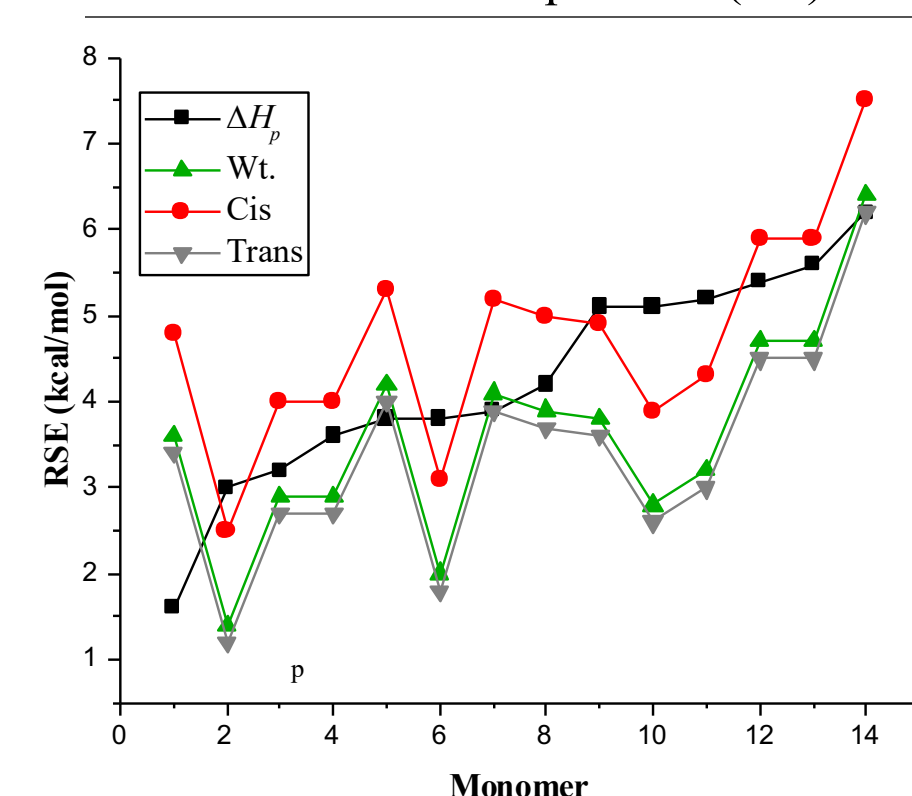| H2 Variant	Wt	Cis	Trans
MAE (kcal/mol)	-0.65	0.47	-0.85
# Monomers > ±1.5 kcal/mol deviation	5	1	5

Figure 3. Commonly used CP Monomers with previously reported experimental ΔH_p values.

b. Previously Reported (H1) vs New Isodesmic Equations (H2_cis)

Isodesmic Equation	H1	H2_cis
MAE (kcal/mol)	1.03	0.47
# Monomers > ±1.5 kcal/mol deviation	4	1

Figure 4. Commonly used CP Monomers with previously reported experimental ΔH_p values.

- Energy cancellation observed when changing olefin conformations in the polymer repeating units.
- RSEs change depending on isodesmic equation.

Isodesmic Equations		RSE (kcal/mol)
a.		7.3
b.	20 % 80 %	6.7
c.		5.9
d.		4.4
Experimental ΔH_p		5.6

Figure 5. Modified **H2_cis** homodesmotic equations for **13** to evaluate *cis:trans* olefin conformational effects in the polymer repeating units.

Isodesmic Equations		RSE (kcal/mol)
a.	OTBS	6.5
b.	OTBS	4.8
c.	OTBS	3.3
Experimental ΔH_p (1)		**1.6**
d.	OTMS	6.7
e.	OTMS	2.5
Experimental ΔH_p (2)		**3.0**
f.	OTES	6.7
g.	OTES	4.9
Experimental ΔH_p (9)		**5.1**

Figure 6. Modified **H2_cis** homodesmotic equations for **1, 2,** and **9** to evaluate *cis:trans* olefin conformational effects in the polymer repeating units.

	CP Derivatives	$\Delta H_{p, exp}$	H1	H2_trans	H2_cis	H2_wt
1	CP2TBS	1.6	5.4	3.4	4.8	3.6
2	CP2TMS	3.0	5.7	1.2	2.5*	1.4
3	CP3MeOH	3.2	(4.5)	2.7*	4.0*	2.9*
4	CP3Ox	3.6	4.3*	2.7*	4.0*	2.9*
5	CP3OBn	3.8	5.7	4.0*	(5.3)	4.2*
6	CP3MeOBn	3.8	3.7*	1.8	3.1*	2.0
7	CP3MeOx	3.9	(5.1)	3.9*	(5.2)	4.1*
8	4CatCP	4.2	5.9	3.7*	5.0*	3.9*
9	CP2TES	5.1	5.7*	(3.6)	4.9*	(3.8)
10	4PCP	5.1	4.8*	2.6	(3.9)	2.8
11	CP3TBS	5.2	5*	3.0	4.3*	3.2
12	CPBIB	5.4	5.9*	4.5*	5.9*	4.7*
13	CP3ol	5.6	5.8*	(4.5)	5.9*	3.7*
14	CP3OH	6.2	6.6*	6.2*	(7.5)	6.4*
	MAE	-	1.03	-0.85	0.47	-0.65
	RMSD	-	1.53	1.39	1.22	1.28

Table 1. Predicted RSE and experimental ΔH_p values (kcal/mol) using different homodesmotic reactions on the lowest energy conformers. Values with an asterisk or parentheses are RSEs within 1 and 1.5 kcal/mol agreement with ΔH_p, respectively. Highlighted values are RSEs > ±1.5 kcal/mol disagreement with ΔH_p.

| Computational Setup		Monomers													Error	
Functional	Basis Set	CP2TBS	CP2TMS	CP3OBn	4PCP	CP3TBS	CP	CP3ol	CP2TES	CP3MeOH	CP3ox	CP3MeOX	P4CatCP	a-BIB	MAE	RMSD
B3LYP	6-31+G*	5.02	5.25	2.87	3.95	4.50	-	8.00	5.25	4.57	4.13	5.51	5.08	6.15	0.83	1.54
B3LYP	6-31+G* in PhMe	4.80	2.50	5.30	3.90	4.30	5.90	7.50	4.90	4.00	4.00	5.20	3.90	5.90	0.47	1.22
B3LYP	6-31+G*-D3	13.55	11.38	10.94	9.54	*	8.82	11.9	13.7	5.22	-	-	-	-	6.42	7.10
B3LYP	6-311++G**	4.54	4.76	2.38	#	4.52	-	7.61	4.75	4.39	3.67	5.11	4.70	5.26	0.58	1.32
B3LYP	6-311++G**-D3	13.08	12.72	10.47	9.28	*	8.42	11.58	13.27	9.50	-	-	-	-	6.83	7.33
B3LYP	aug-cc-pVDZ	5.70	3.40	3.51	-	5.63	#	#	5.81	5.22	4.71	*	5.65	6.23	1.19	1.69
B3LYP	aug-cc-pVDZ-D3	14.33	12.35	11.68	10.77	15.68	9.41	-	14.51	10.42	-	-	-	-	8.31	8.71
B3LYP	aug-cc-pVQZ	*	*	#	*	*	*	*	*	-	*	*	*	-	-	-
B3LYP	aug-cc-pVQZ-D3	#	#	#	*	#	*	#	-	#	-	-	-	-	-	-
B3LYP	def2-SVPD	6.38	6.01	4.51	#	5.98	6.63	9.61	8.47	6.79	5.15	6.62	5.87	7.09	2.35	2.66
B3LYP	def2-SVPD-D3	14.91	13.28	12.62	10.67	15.97	9.41	13.81	15.01	12.34	-	-	-	-	8.79	9.19
B3LYP	def2-QZVPD	3.73	0.91	1.76	*	3.43	-	#	3.93	-	3.40	4.77	-	-	-0.62	1.62
B3LYP	def2-QZVPD-D3	12.01	8.74	9.90	*	12.83	8.16	11.30	12.02	-	-	-	-	-	6.34	6.72
	Experimental ΔH_p	1.63	3.02	3.84	5.10	5.22	5.60	6.20	5.08	3.20	3.56	3.93	4.20	5.40	-	-

Table 2: Predicted RSE values B3LYP with and without the D3 dispersion correction with various basis sets. All values given in kcal/mol. Symbols represent common errors such as memory (*) and convergence (#), and (-) are calculations still in progress.

Discussion

Overall, extra computational cost and time resulted in diminishing returns. When considering various conformers, H2_cis using the lowest energy conformers is the optimal and recommended method. The design of the isodesmic equation most accurately represents ROMP and yielded good absolute values (MAE= 0.47 and RMSD= 1.22 kcal/mol) using considerably less computational time, cost, and space. Similarly, B3LYP paired with the Pople basis sets provided the most accurate results in the shortest time with the least memory issues and convergence errors. The extra computational time and cost of using the dispersion correction consistently resulted in greater MAE and RMSDs compared to ΔH_p. This is likely due to an inequivalent correction to mid-range electron correlation energies between the monomer and repeating unit. Therefore, B3LYP/6-31+G* in a toluene PCM and B3LYP/6-311++G** are recommended for future RSE predictions.

Summary and Future Work

B3LYP with the Pople basis sets provides reasonable accuracy with low computational time and cost required future and is recommended for RSE predictions. Structural analyses will be performed on several CP derivatives to identify if and what structural relationships exist with RSEs. A better understanding RSE and how structural features affect these energies can facilitate experimental design of novel materials potentially capable of CRM. Not only can this information help monomer design, but also streamline the identification of optimal reaction conditions.
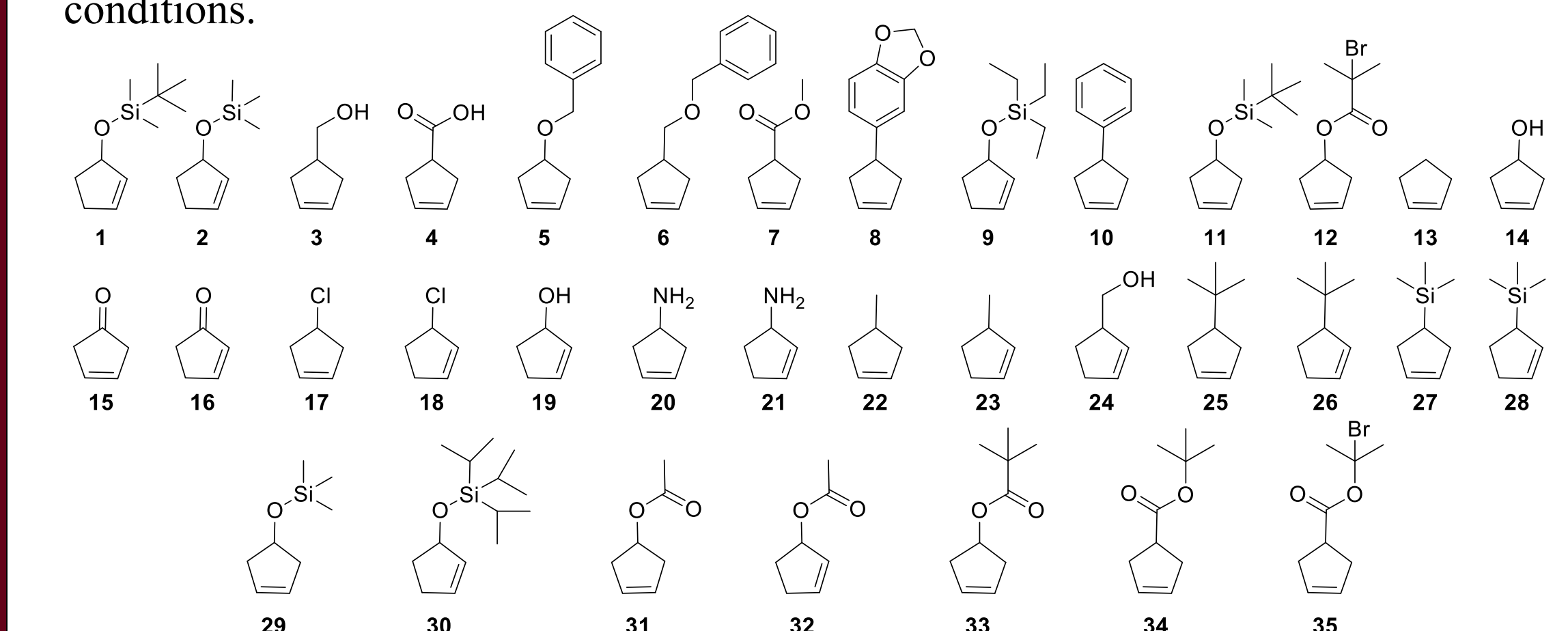
Scheme 3: Monomers being used to determine structural relations to RES such as Olefin and substituent hybridizations, Olefin natural charge, substituent nature, substituent location, and steric bulk.

Acknowledgements

References

1. R. Geyer, J. R. Jambeck and K. L. Law, *Science Advances*, 2017, 3, e1700782.
2. G. W. Coates and Y. D. Y. L. Getzler, *Nature Reviews Materials*, 2020, 5, 501-516.
3. W. J. Neary and J. G. Kennemur, *ACS Macro Letters*, 2019, 8, 46-56.
4. B.M. Coia, S.E. Werner, J.G. Kennemur. *In Preparation.* 2022.