

Chapter 1

Introduction to Cyclic Polymers and Olefin Metathesis

Cyclic Polymers

Cyclic polymers have drawn considerable interest for their distinct physical properties relative to analogous linear polymers, despite their equivalent chemistries. This divergence in material properties originates entirely from their divergent topologies. The mobility of chain-ends in linear polymers determines their propensity for chain-entanglement, whereas the absence of chain-ends in cyclic polymers engenders comparatively lower propensities for chain-entanglement. Additionally, the inherent restriction of cyclic polymer elongation produces densities, conformations, and viscoelastic properties unique to their topologies in all physical states. Exploitation of these fundamental differences through a cyclic topology-selective synthetic methodology affords distinct material properties from an analogous linear synthetic methodology, but without modification of monomer composition or MW distribution¹⁻⁶ (Table 1).

Table 1 | The discrepancies in physical properties of cyclic versus linear polymers. (R_h = hydrodynamic radius, T_g = glass transition temperature).

Property	Linear Polymer	Cyclic Polymer
Intrinsic Viscosity	higher	lower
Melt Viscosity	higher	lower
Solution Conformation	random coil	discotic
R_h	higher	lower
T_g	lower	higher

The most common methods for the synthesis of cyclic polymers are a) ring-closure of a telechelic linear polymer and b) ring-expansion, where the cyclic topology of the growing polymer chain is preserved throughout (Figure 1).¹⁻³ Significant limitations and advantages exist for both methods. The requisite high dilution for ring-closure methods foments a number of fundamental problems: gram-scale quantities are infeasible, high MWs are inaccessible, and ring concatenation is inevitable. However, since ring-closing reactions are often carried out with telechelic polymers prepared by living methods, the resulting cycles can have low \bar{D} .^{4,5} Additionally, there are many more ring-closure synthetic strategies, so diversity in monomer scope is common.

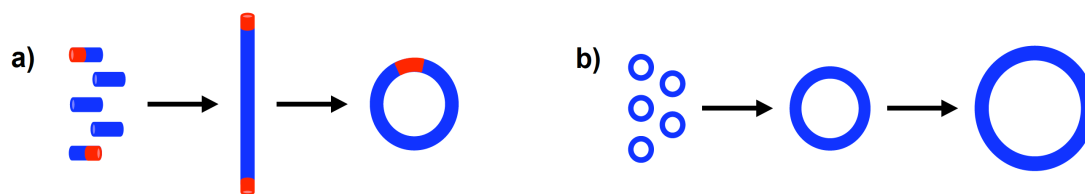


Figure 1.1 | Ring-closure (a) and ring-expansion (b) routes to cyclic polymers.

Ring-expansion of cyclic polymers is a newer method that is being explored by a number of groups. Ring-expansion polymerizations can be conducted on a more useful scale because they do not require high dilution, though they typically suffer from broad \bar{D} . Additionally, ring-expansion produces polymers with uniform chemical composition, unlike the cycles formed using ring-closure of telechelic chains that possess at least one condensed telechelic moiety per chain.^{5,7} Larger quantities of cyclic material than are generally accessible

through ring-closure methods are required to study melt-state properties because of the sample sizes required — e.g., differential scanning calorimetry (DSC), and especially rheology.

Existing studies on the rheological properties of cyclic polymers have not been in complete agreement. This is generally thought to be a result of both broad dispersity of the bulk material and the presence of linear polymer impurities. These undesirable features negatively impact analysis of melt-state material due to irreproducibility and convoluted data interpretation.⁸ A method to synthesize cyclic polymers free of linear impurity at scale and with MW control (including MWs above 100 kg/mol), low \bar{D} , and functional-group-tolerance of diverse monomer compositions remains elusive, but would dramatically increase our understanding of cyclic polymer material properties and synthetic strategies.

The lack of agreement among the polymer synthesis and polymer physics communities in regards to the properties of cyclic polymers comes, in large part, from linear polymers present in cyclic samples. Rheology of cyclic polymers is particularly challenging, because even minuscule levels of linear impurity nullify their peculiar viscoelastic properties. Using common rheology techniques, samples of cyclic polymers containing less than 0.07 wt.% linear impurity leads to inadequate data.⁹

Recent developments in cyclic polymer synthesis

Cyclic polymer synthetic methodology has been continually expanding and improving, particularly in the past 5 years. One notable example of a ring-closing

technique was reported for the ROP of γ -butyrolactone. Through judicious control of catalyst design and conditions, both cyclic and linear poly(γ -butyrolactone) with MWs exceeding 30 kDa were accessible. Notably, they found the cyclic polymer to be considerably more stable than its linear analog during the thermal depolymerization process used to recycle the monomer (Fig 1.2).¹⁰

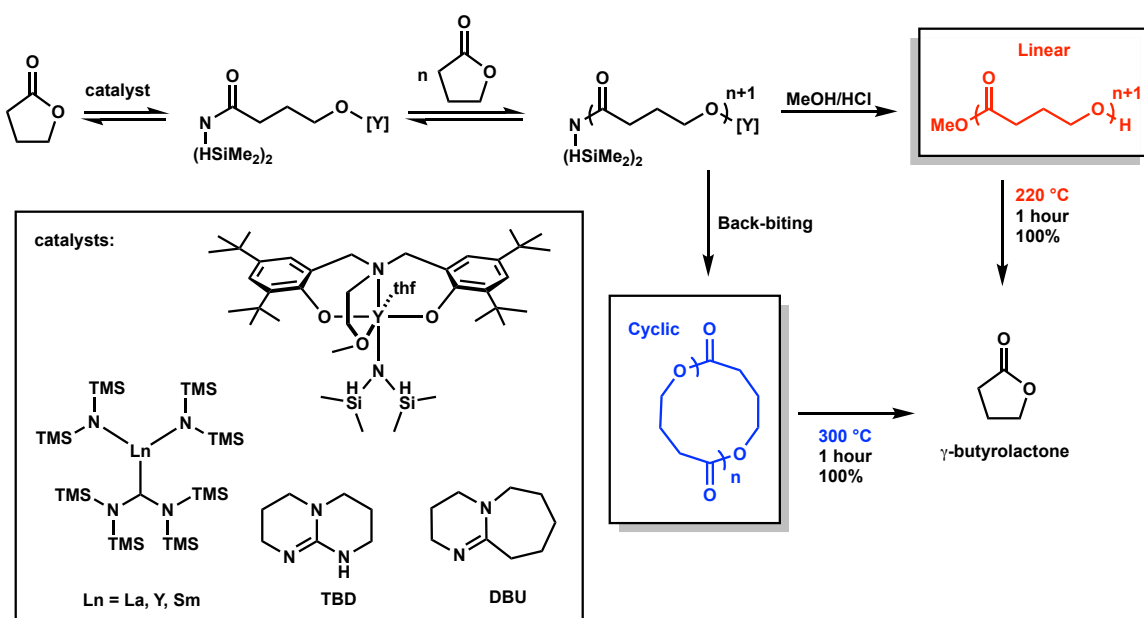


Figure 1.2 | Cyclic poly(γ -butyrolactone) synthesis and depolymerization recycling process.

Some work using zwitterionic ring-opening polymerization (ZROP) has also garnered attention. In ZROP, an N-heterocyclic carbene (NHC) is used to ring-open a lactone or lactide monomer and the electrostatic attraction between the two chain ends provides a cyclic topology upon release of the NHC (Fig 1.3).^{1,7,11}

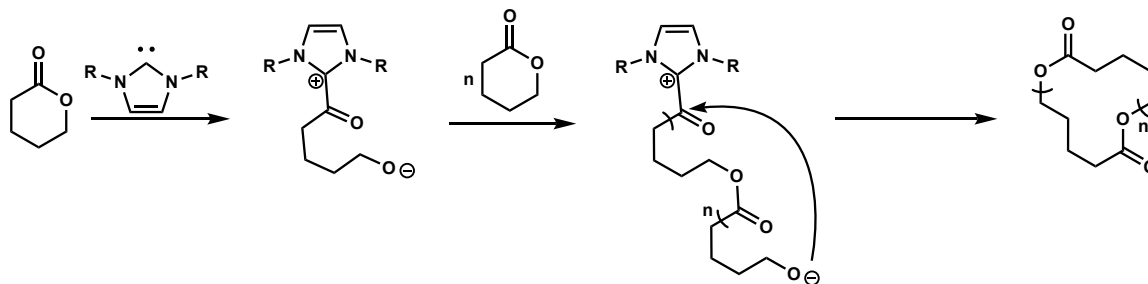


Figure 1.3 | Zwitterionic ring-opening polymerization (ZROP) of δ -valerolactone.

Radical addition-fragmentation polymerization (RAFT) is a powerful method to prepare polymers in a living fashion. It has also been used to prepare cyclic polymers from monomers such as N-vinyl carbazole using a cyclic RAFT initiator (Fig 1.4).¹²

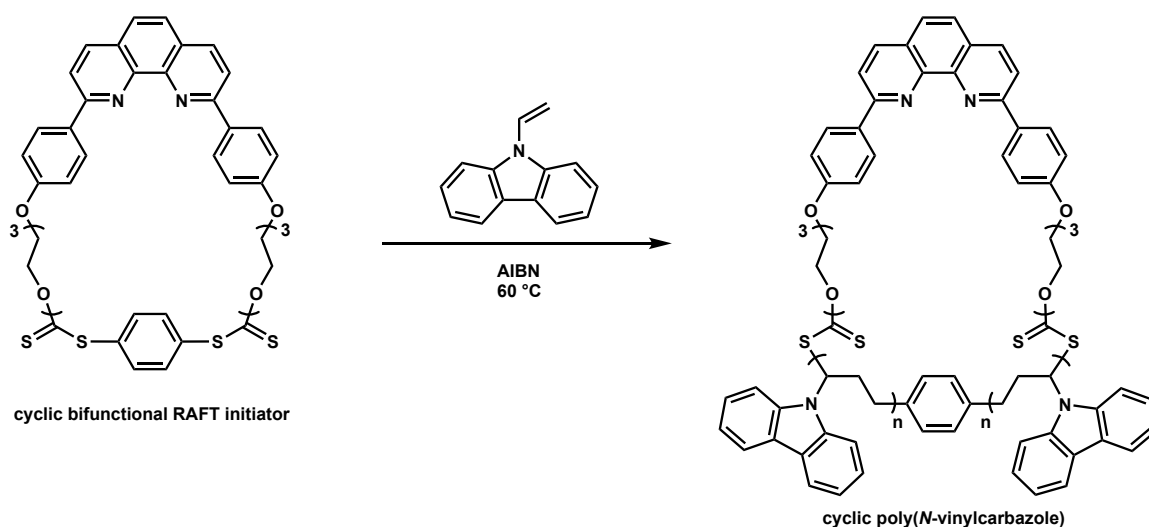


Figure 1.4 | Cyclic poly(*N*-vinylcarbazole) using a bifunctional RAFT initiator.

Determining cyclic polymer purity

Assessing the purity of cyclic polymers presents a challenge equal to the synthesis itself. The only compositional discrepancy between cyclic and linear is the latter's end-groups, but the concentration of end-groups in linear polymer chains often falls below the detection limit of conventional spectroscopic methods. However, a few powerful techniques for measurement of cyclic purity do exist: viscometry for intrinsic viscosity, rheology for melt-state viscoelasticity, and interaction chromatography (IC) for molecular homogeneity.¹³

The different intrinsic viscosities of cyclic and linear chains with equivalent MW can be useful to qualitatively assign a cyclic topology, but this method cannot quantify linear impurity. Rheology is the most sensitive analytical technique: 0.07% (w/w) linear impurity can be reliably detected. Kapnistos et al. observed significant differences in the stress relaxation modulus between linear poly(styrene) (PS), cyclic PS made by a ring-closure method, and the same cyclic PS after purification by IC (Fig 1.5, left).⁹ They observed the characteristic entanglement plateau at intermediate relaxation times ($10^{-3} < t \text{ (s)} < 10^0$) for linear PS. However, during the same intermediate relaxation time, an "extended relaxation regime" was observed for cyclic PS. The intermediate curve for unpurified rings (red, Fig 1.5) corroborates the suspicion that cyclic polymers free of linear impurity are exceptionally rare. They also intentionally mixed linear chains with cycles and studied the relaxation behavior based on the weight fraction of added linear chains (Fig 1.5, right). This demonstrated the incredible power of

rheology to assess purity of cyclic polymers, but also revealed the vital importance of IC in the field of cyclic polymers—these findings would not have been possible without cyclic PS purified through preparative IC.

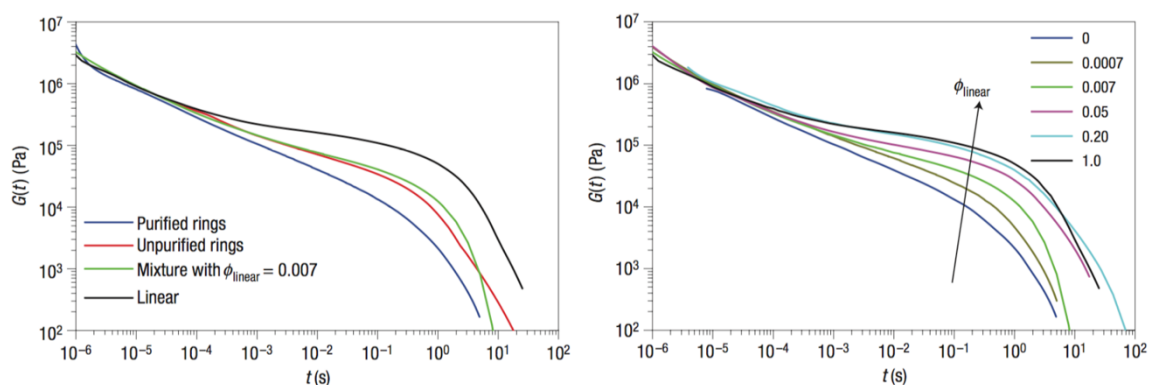


Figure 1.5 | Stress-relaxation modulus for cyclic and linear PS (left) and the effect of linear impurity on the stress-relaxation dynamics of cyclic PS (right). Reproduced from Kapnistos et al.⁹

Macromolecules with distinct molecular compositions, but otherwise similar physical properties, can be separated, quantified, and purified with IC. The success of IC with cyclic polymers has been well demonstrated, although there is disagreement as to the thermodynamic parameters underlying this success. Nevertheless, separation of macromolecules by topology can be achieved with IC, so direct measurement of cyclic and linear chains can be made.

Olefin Metathesis

Olefin metathesis emerged as one of the most powerful carbon-carbon bond forming reactions available in chemical synthesis in the 1980's and 1990's when R.H. Grubbs (Caltech) and R.R. Schrock (MIT) developed the first well-defined olefin metathesis catalysts. Their work confirmed the mechanism

originally proposed by Y. Chauvin (IFP) decades prior. The three shared the Nobel Prize in Chemistry in 2005 for their contributions to the olefin metathesis reaction.

Schrock developed many types of metathesis catalysts based on tungsten (W) and molybdenum (Mo)(**1.0–1.2**, Fig 1.6). Grubbs then followed with a number of catalysts based on ruthenium (Ru)(**1.3–1.8**, Fig 1.6). Grubbs-type catalysts are generally more stable, whereas Schrock-type catalysts are generally more active. This maxim was particularly accurate in the early days of metathesis, although the Grubbs-type catalysts are still more bench-stable and rarely require storage in inert atmosphere or reduced temperature, unlike the Schrock-type catalysts.

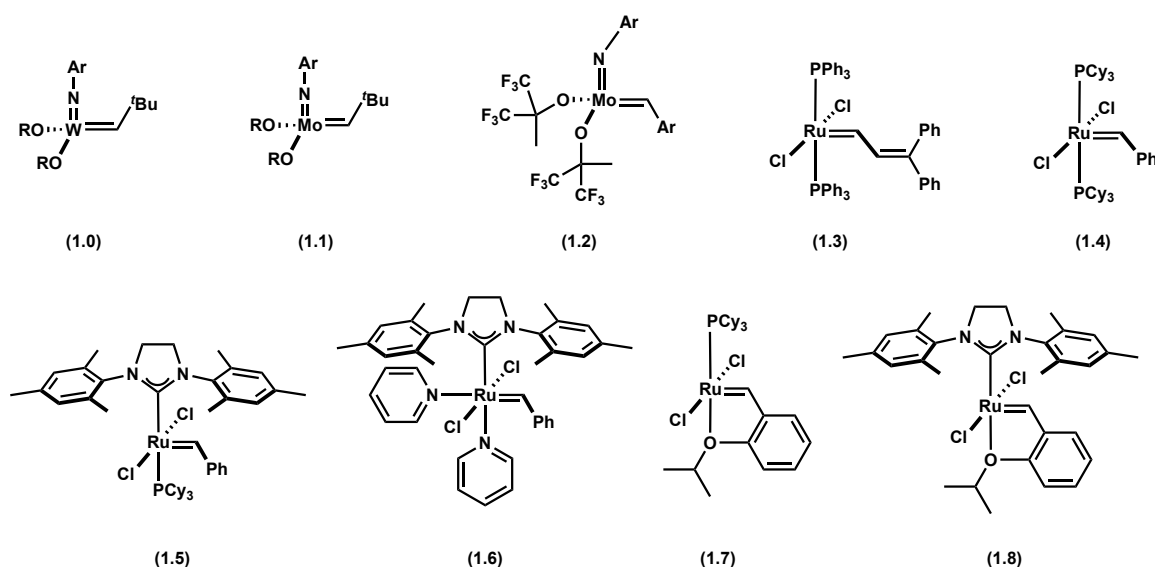


Figure 1.6 | Common olefin metathesis catalysts based on W (**1.0**), Mo (**1.1–1.2**), and Ru (**1.3–1.8**).

A carbene—a metal-carbon double bond—is the unifying feature of olefin metathesis catalysts (Fig 1.7, **1.9**). The metathesis catalytic cycle begins when an olefin (**1.10**) coordinates to the metal center (**1.11**) and undergoes a [2+2]

cycloaddition to form a metallocyclobutane intermediate (**1.12**). The subsequent cycloreversion rearranges the carbon-carbon bonds to form an olefinic product (**1.13**) bearing the functional group previously bound to the metal center (R). This forms a ruthenium-carbon double bond with new substituents (**1.14**). The metathesis reaction continues with substrates bearing different substituents (**1.15**) which undergo the [2+2] cycloaddition and cycloreversion step (**1.16**) which ultimately leads to the metathesis product (**1.17**), which is an olefin substituted with a combination of the original substrates' substituents (**1.10** and **1.15**).

The metathesis activity of early catalysts was generally verified by their ability to ring-open norbornene, a reactive bicyclic olefin with high ring-strain (28 kcal/mol). Metathesis catalysts gradually improved, becoming more stable and more active, such that many other types of olefin metathesis reactions for small-molecule synthesis (Fig 1.8, left) and polymerization (Fig 1.8, right) became viable.

The scope of transformations that metathesis catalysts were able to perform became expansive (Fig 1.3): ring-closing metathesis (RCM), cross metathesis (CM), ring-opening cross metathesis (ROCM), alkyne metathesis (AM), enyne metathesis (EYM), ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET), ring-closing enyne metathesis polymerization (RECEYMP), and ring-expansion metathesis polymerization (REMP). These

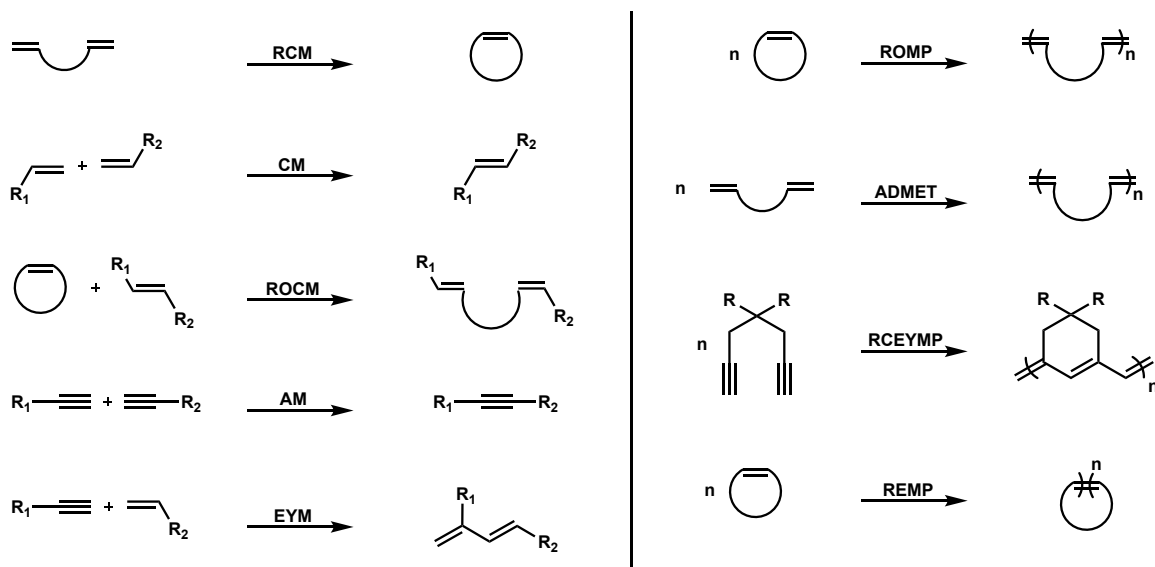


Figure 1.8 | Common types of olefin metathesis reactions for small-molecule synthesis (left) and polymer synthesis (right).

The utility of ROMP in polymer chemistry cannot be overstated. ROMP provides functional group tolerance, MW control, low \bar{D} , and architectural control, particularly when using Grubbs-type ruthenium-based catalysts.¹⁴ The mechanism of ROMP (Fig 1.5) is consistent with its living nature and ability to control MW through $[\text{monomer}]_0:[\text{catalyst}]_0$ loadings, whereby each catalyst produces one chain by chain-growth.

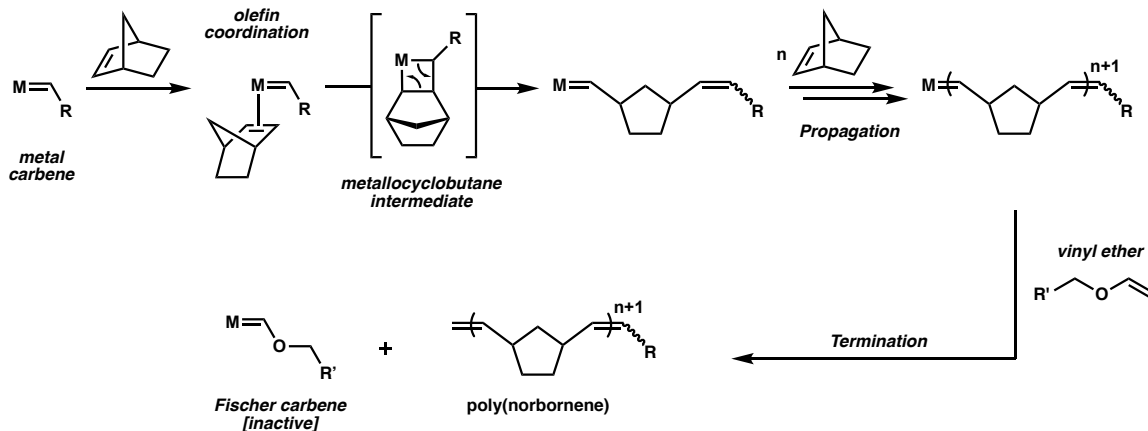


Figure 1.9 | The mechanism of ROMP for norbornene.

These desirable features do require, however, a cyclic olefin monomer with high ring-strain. High ring-strain monomers provide ROMP polymers with the best MW control and \bar{D} because secondary metathesis events which increase \bar{D} through back-biting and chain-transfer cannot occur. Although low ring-strain monomers can be polymerized, they are generally more difficult to polymerize in a controlled fashion (Fig 1.10). The ring-strain necessary for ROMP is approximately 5 kcal/mol because the entropic penalty is approximately 5 kcal/mol. That is, the enthalpy of ring-opening the monomer must compensate for the entropic cost of polymerization. A consequence of these basic thermodynamic principles is that the critical monomer concentration (CMC) must be exceeded for ROMP to be spontaneous, so for low- and intermediate- ring-strain monomers, concentrations above 1.0 M are generally required. The CMC for high ring-strain monomers, such as norbornene, is negligibly small.

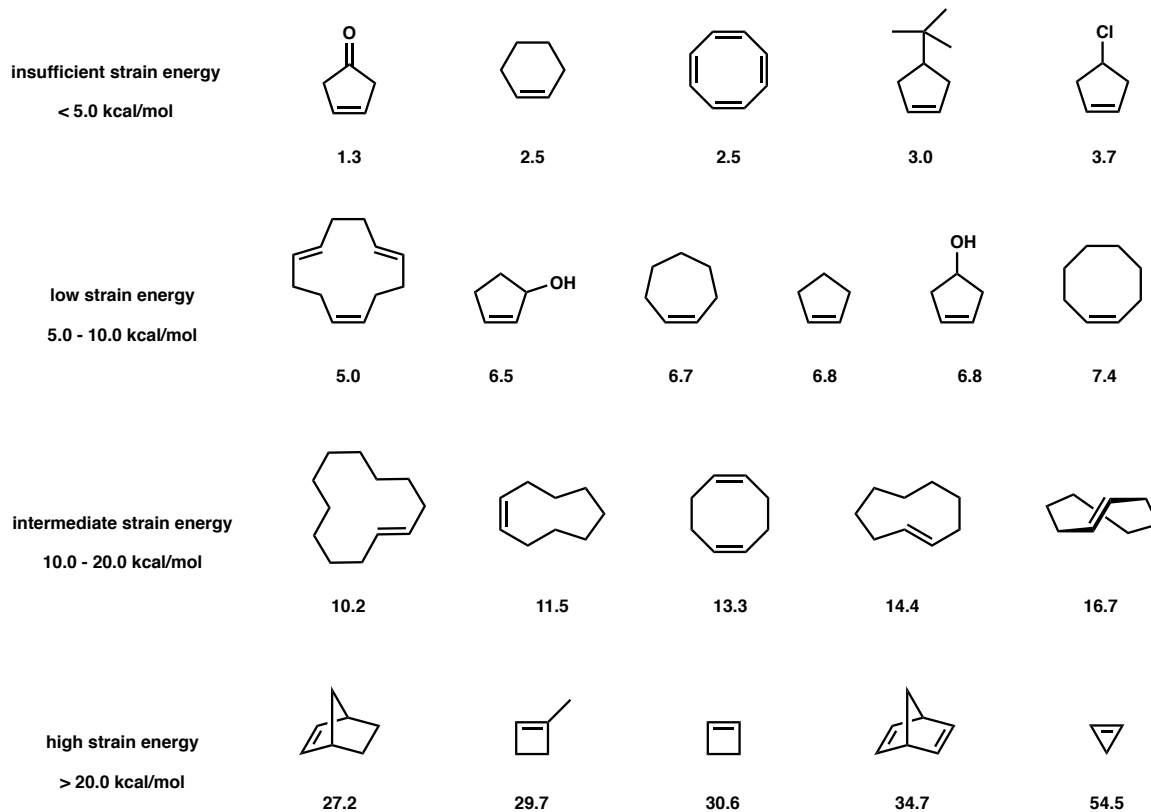


Figure 1.10 | Monomers unsuitable for ROMP (top row) and monomers with ring-strain sufficient for ROMP (bottom rows).

References

- (1) Brown, H. A.; Waymouth, R. M. *Acc. Chem. Res.* **2013**, *46* (11), 2585–2596.
- (2) Zhu, Y.; Hosmane, N. S. *ChemistryOpen* **2015**, *4* (4), 408–417.
- (3) Kricheldorf, H. R. *Journal of Polymer Science Part A: Polymer Chemistry* **2009**, *48*, 251–284.
- (4) Xia, Y.; Boydston, A. J.; Yao, Y.; Kornfield, J. A.; Gorodetskaya, I. A.; Spiess, H. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131* (7), 2670–2677.
- (5) Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009**, *38* (8), 2202–2213.
- (6) Nasongkla, N.; Chen, B.; Macaraeg, N.; Fox, M. E.; Fréchet, J. M. J.; Szoka, F. C. *J. Am. Chem. Soc.* **2009**, *131* (11), 3842–3843.
- (7) Chang, Y. A.; Waymouth, R. M. *Journal of Polymer Science Part A: Polymer Chemistry* **2017**, *55* (18), 2892–2902.
- (8) McKenna, G. B.; Hostetter, B. J.; Hadjichristidis, N.; Fetters, L. J.; Plazek, D. J. *Macromolecules* **1989**, *22* (4), 1834–1852.
- (9) Kapnistos, M.; Lang, M.; Vlassopoulos, D.; Pyckhout-Hintzen, W.; Richter, D.; Cho, D.; Chang, T.; Rubinstein, M. *Nat Mater* **2008**, *7* (12), 997–1002.
- (10) Hong, M.; Chen, E. Y. X. *Nature Chemistry* **2016**, *8* (1), 42–49.
- (11) Culkun, D. A.; Jeong, W.; Csihony, S.; Gomez, E. D.; Balsara, N. P.; Hedrick, J. L.; Waymouth, R. M. *Angew. Chem. Int. Ed.* **2007**, *46* (15), 2627–2630.
- (12) Bunha, A.; Cao, P.-F.; Mangadlao, J. D.; Advincula, R. C. *Reactive and Functional Polymers* **2014**, *80*, 33–39.
- (13) Lee, H. C.; Lee, H.; Lee, W.; Chang, T.; Roovers, J. *Macromolecules* **2000**, *33* (22), 8119–8121.
- (14) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**.