ACS Macro Letters
Viewpoint
Cite This: ACS Macro Lett. 2019, 8, 46−56
pubs.acs.org/macroletters

Polypentenamer Renaissance: Challenges and Opportunities

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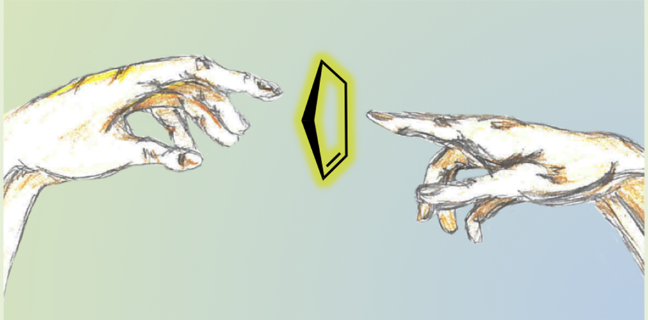


ABSTRACT: This Viewpoint highlights the viability and increasing variety of functionalized polypentenamers as unique and valuable materials created through enthalpy-driven ring-opening metathesis polymerization (ROMP) of low ring strain cyclopentene monomers. The terms “low ring strain” and “enthalpy-driven” are typically conflicting ideologies for successful ROMP; however, these monomers possess a heightened sensitivity to reaction conditions, which may be leveraged in a number of ways to provide performance elastomers with good yield and precise functional topologies. Over the last several years, a rekindled interest in these systems has led to a renaissance of research aimed at improving their synthesis and exploring their potential. Their chemistry, applications, and future outlook are discussed.

The field of polyolefins is seeded in even-integer branch topologies where vinyl, diene, and α-olefin monomers propagate exactly 2 or 4 additional carbons with each repeating unit. Copolymerization with ethylene to increase branch distances only continues to proliferate an even-numbered spacing while lacking sequence precision. When thinking about our current understanding of the structure−property relationships for polymeric systems, the odd-numbered branch topology is significantly less explored. The interest in such materials may be rationalized by the influences of the odd−even effect in a multitude of phenomenologies throughout chemistry.[1] A great example of odd−even effects in polymer science can be found from polycondensation polymers featuring varying lengths of aliphatic segments within the comonomers used.[2] Their semicrystalline melting temperatures can vary considerably if these segments contain an odd or even number of carbons.[2] Similarly, the 2-carbon branch topology of isotactic and syndiotactic polyolefins is known to provide a rich variety of semicrystalline polymers;[3,4] it begs the question of how crystalline properties would change if an isotactic branch was spaced every three carbons? Every five? The influence of odd−even effects on polymers may stretch even further than systematic crystalline packing. For example, *n*-alkanes, the most fundamental platform for studying odd−even effects, have been recently found to undergo dynamic changes in their translational diffusion just above the melting point.[5] These changes depended on even- or odd-numbered carbons within a homologous series.[5] Would amorphous polymer melts also be susceptible to differences in thermal and dynamic quantities resulting from odd or even branch spacing? To answer these questions, in addition to exploration of completely new materials, access to precise microstructures that feature the odd-branch spacing is needed.

Ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization are powerful methods for producing polyalkenamers with a variety of chemistries, branch periodicities, and architectures.[6−9] Substituents on odd-numbered cycloolefin rings or α,ω-dienes can produce odd-numbered, and potentially precise, branch topologies, while subsequent hydrogenation of the backbone olefins produces linear polyethylene analogues. This Viewpoint will focus on the five-carbon topology (polypentenamers) which has historically presented synthetic challenges for both ADMET and ROMP. Recent progress in the field of polypentenamers reveals promise to overcome many of these hurdles and introduces an almost unexplored variety of precision materials. A scope of the frontlines and a viewpoint of future needs are discussed.

Challenges with ADMET. A large variety of precision polyolefins with odd-branch spacing have been successfully reported from ADMET polymerization of large linear α,ω-dienes.[8,10,11] After hydrogenation, many of these materials feature large “runs” of polyethylene with precise (or purposefully imprecise) branches, making ADMET an ideal tool for exploring crystallization behavior from varying distances along the chain.[8,11−13] However, polypentenamers from ADMET of 1,6-heptadienes present significant challenges over the much larger α,ω-diene monomers typically used.[8] The first stems from the Carothers equation for step-growth polymerizations where smaller monomers will require a more stringent extent of reaction to obtain higher molar mass.[14] To target a polypentenamer with a number-average molar mass (M_n) of ~52 kg mol^{-1}, approximately 9,987 out of every 10,000 monomer olefins on 1,6-heptadiene (accounting for the loss of ethylene) would need to be successfully polymerized. This assumes that no cyclization products are occurring and

Received: November 15, 2018
Accepted: December 12, 2018
Published: December 20, 2018

ACS Publications

DOI: 10.1021/acsmacrolett.8b00885

segues into the biggest challenge with ADMET: cyclization of 1,6-heptadienes into cyclopentene is a highly competitive side reaction.[8] For example, Li et al. recently reported that ADMET of 4-acetoxy-1,6-heptadiene at 60 °C produced 4-acetoxycyclopentene as the only product.[15] Ring-closing metathesis (RCM) over ADMET is favorable due to the low ring strain of cyclopentene and is also bolstered by Thorpe−Ingold effects.[16] As will be discussed, this attribute is also a key challenge in the efficacy of ROMP. An alternative strategy was reported by Baughman et al. where 4,9-dimethyldodeca-1,11-diene polymerizes into a 10-carbon repeating unit with atactic methyl branches judiciously placed at every fifth carbon following hydrogenation.[17] One of the defining features of this polymer was that it was amorphous, unlike when an atactic methyl branch is placed at every 7 carbons.[17] Therefore, the five-carbon periodicity is positioned to produce amorphous precision polyolefins, which are far less researched. A substantial limitation of this approach was the laborious multistep and low-yielding synthesis of 4,9-disubstituted α,ω-dodecadienes. No other materials featuring a five-carbon branch periodicity from ADMET have followed.

ROMP and Ring Strain. ROMP has gained considerably more interest as a means to access polypentenamers. The equilibrium chain-growth mechanism of ROMP also presents the opportunity for living-like character (targeted molar mass and narrow dispersity ($Đ$)), which has been realized over the last several decades through continuous catalyst development and optimization of reaction conditions.[6,18−21] During this maturation, the use of high-strain bicyclic or cyclic monomers (e.g., norbornenes (NB)s, oxanorbornenes (ONB)s, cyclobutenes (CB)s, etc.) has yielded high conversions at common temperatures (20−80 °C).[6] These monomers circumvent challenges associated with the equilibrium mechanism which is driven by the release of their high ring strain. Earlier work by the Schrock group,[22,23] and more recently by the Xia group,[24] has shown success in producing a three-carbon repeating unit from substituted and highly strained cyclopropenes, which is ushering in new opportunities to explore the 3-carbon topology. Our group, and others discussed herein, has been focusing on the 5-carbon topology. Before discussing polypentenamers, it is necessary to first consider why cyclopentenes have been historically challenging. Figure 1a displays ring strain values of cycloalkanes (bars) and cycloalkenes (lines) when traversing the number of carbons in the ring (n). A reduction in ring strain directly correlates to a reduction in the absolute value of the enthalpy of polymerization (ΔH_p) and therefore challenges the exergonic character of ROMP in accordance to the Gibbs free energy equation of equilibrium polymerization (eq 1).

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (1)$$

Increasing n from 3 to 12 results in significant changes in the overall ring strain. The source of strain traverses bond angle (Baeyer) strain (n = 3, 4), torsional (Pitzer) strain (n = 5, 6), and *trans*-annular (Prelog) strain (n > 6).[25] Cyclohexene has a negligible ring strain (<10.5 kJ mol^{-1})[26] and, coupled with the entropic penalty associated with polymerization, has a very low ceiling temperature ($T_c < -116$ °C at 7.5 M).[27] The entropy of polymerization (ΔS_p) also plays an important role with increasing n. The general trend is that the entropic penalty associated with ROMP decreases as rings become larger and benefit more from gaining conformational entropy in the ring-opened state. At very large and unstrained ring sizes ($n \geq \sim$ 14), ROMP can be entirely driven by entropy.[28−30] Furthermore, the *trans*-annular strain of *cis*-cyclooctene is quite low ($-\Delta H_p \approx 31.0$ kJ mol^{-1}),[31] yet these monomers polymerize readily due to a favorable entropic penalty ($-\Delta S_p \approx 9$ J K^{-1} mol^{-1}).[32] Cyclopentene (CP) benefits from neither a high strain nor a favorable entropy ($-\Delta S_p \approx 70 \pm 6$ J K^{-1} mol^{-1})[33−35] which underpins the challenge to produce polypentenamers to appreciable conversions.[36] As seen in Figure 1b, the strain of cyclopentane is mostly torsional due to the unfavorable eclipsed conformation of substituents from neighboring ring carbons. For CP (Figure 1c), the planarity of the olefin reduces the total quantity of eclipsed hydrogens and helps explain why CP is a hyperstable olefin (i.e., CP is *less* strained than cyclopentane) even though the sp^2-hybridized carbons are experiencing higher angular strain.[25] Building on this, one can hypothesize an improvement of CP torsional strain through the use of bulkier substituents on the 3, 4, or 5 position of the ring; however, this idea works in opposition to Thorpe−Ingold or *gem*-dimethyl effects upon ring opening, making definitive predictions on the efficacy of ROMP on substituted CP derivatives an ongoing challenge.[37−39] As seen in eq 1, a reduction in the absolute value of ΔH_p results in a heightened importance and sensitivity that reaction temperature (T) has on ΔG_p. Therefore, reduced T coupled with other important dynamic equilibrium parameters (monomer concentration or pressure) all stand to play a vital role in the efficacy of successful ROMP for low strain species. This is an important concept suggesting high conversions are possible through the modification of reaction conditions outside those typically used for ROMP of higher strain monomers.

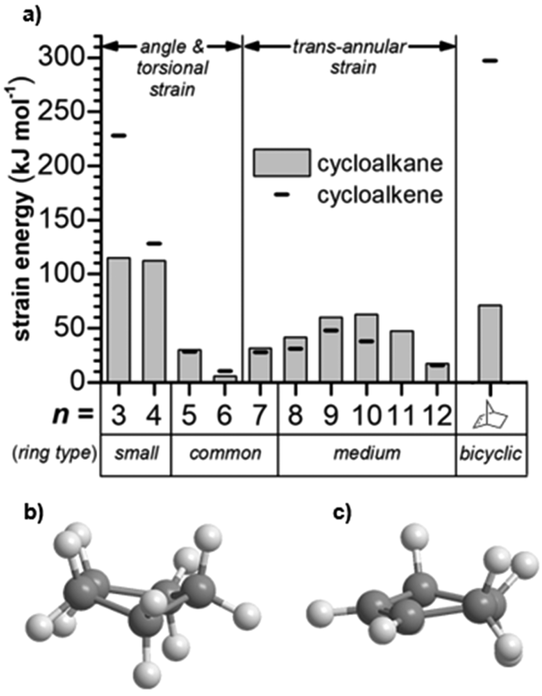


Figure 1. (a) Ring strain energy values for cyclic alkanes (bars) and alkenes (dashes) with varying number of ring carbons (n) from 3 to 12. Ball−stick 3D renderings of cyclopentane (b) and cyclopentene (c) illustrate the sources of torsional (eclipsed) strain and hyperstability of the alkene. Strain values were gathered from refs 25 and 26.

Early Discoveries of PCP. The sentiment of "polypentenamer renaissance" stems from the fact that ring-opening polymerization on CP dates back to the discoveries of Herbert Eleuterio (DuPont) in 1957.[40] Over the next decade, this field was heavily researched by Dall'Asta (Montedison), Natta (Montedison), Ofstead (Goodyear), Calderon (Goodyear), and Uraneck (Phillips), to name a few.[4] Specific interest in this polypentenamer (PCP), also described as poly(1-pentenylene), was a result of the natural rubber shortages during WWII. Many early patents and papers were focused on the physical and mechanical properties of PCP with varying *cis*/*trans* content and its inherent similarities to natural rubber. Of particular note are its self-reinforcing properties (crystallization upon strain), low crystalline melting point (T_m = 23 °C) of the *trans*-polypentenamer, and robust cold-temperature performance.[4] While this early work helped shape the utility of ROMP on CP, industrial scaling of these polymers was never brought to fruition (although pilot plants were in place) due to steep economic costs of obtaining cyclopentene from cyclopentadiene at the time.[4]

Research on PCP largely subsided until the late 1980s when well-defined metal carbenes (i.e., "Schrock-type" Mo and W or "Grubbs-type" Ru) led to the mechanistic understanding of the metathesis reaction proposed by Chauvin[41] and the eventual maturation of ADMET and ROMP. During this time, CP and functional derivatives took a backseat to higher ring-strain alternatives, but nevertheless, piecemeal reports began to elucidate their efficacy and potential. Schrock et al. reported ROMP of CP from W(CH-*t*-Bu)(*N*-Ar)(O-*t*-Bu)$_2$ catalyst and achieved high monomer conversion (95%) at −40 °C at an initial monomer concentration (M_0) of 3.4 M in toluene.[35] Dispersities ($Đ$) of PCP were notably less at −40 °C (<1.23) than at 25 °C (>1.5), suggesting better control at lower temperatures. Similar results were reported by Dounis et al. using the same catalyst.[42] Register and co-workers reported a series of PCP and PCP-containing block copolymer (BCP) investigations using Mo(CH-Me$_2$Ph)(*N*-Ar)(O-*t*-Bu)$_2$ catalyst. Trzaska et al.[43] first showed this catalyst is capable of producing narrow $Đ$ of PCP through the use of an auxiliary ligand, trimethylphosphine (PMe$_3$), earlier used by Wu et al.,[44] that effectively reduces propagation rate with respect to initiation rate at room temperature. Hydrogenation of this PCP produced narrow $Đ$ and perfectly linear polyethylene. This was further explored by Myers et al. as a segment in BCPs with polystyrene (PS)[45] or hydrogenated PNB.[46] Although PMe$_3$ helps moderate initiation over propagation, the chain-transfer reactions with internal olefins are still prominent and required termination at low conversions ($\leq$ ~30%)[42,43] where the concentration of internal olefins remains low. Lee et al.[47] determined the rate of propagation to be 1600-fold faster than chain transfer, suggesting that manipulation of experimental conditions may reduce unwanted side reactions. This has recently been revisited and is discussed in the next section.

Exploration on PCP using Ru-based catalysts was scarce during the maturation of ROMP, and typically CP was explored as one of several monomers when determining the performance of new Grubbs catalysts.[48] Hejl et al. were the first to devote an experimental study to Ru-ROMP of low strain monomer species, which included CP and cycloheptene (CHp) derivatives using Grubbs first (G1), second (G2), and third (G3) generation catalysts.[49] Specifically for CP, the outcomes were consistent with equilibrium thermodynamics; bulk polymerizations (11.3 M) at 25 °C produced the highest conversion (~85%), while dilution with CH$_2$Cl$_2$ resulted in less yield at the same temperature. It was also noted that G3 catalyst is sparingly soluble in neat CP, resulting in reduced performance. Nearly all of the polymerizations produced $Đ \geq 1.5$ regardless of dilution or catalyst choice. More recently, Tuba and Grubbs revisited ROMP of CP and explored lower temperatures for the first time while using Hoveyda−Grubbs second-generation catalyst (HG2).[34] Lower temperatures (0 °C) resulted in high conversion (82%) even when moderately diluted (2.17 M) in toluene. However, resulting molar masses were much higher than theoretical, and high $Đ$ (>1.7) was consistently produced. Here we note that, although the choice of catalyst will affect the initiation and propagation kinetics, monomer conversions should, in theory, be independent of catalyst and largely dependent on M_0 and temperature.[36]

Synthetic Advancements for PCP. Aside from typical conditions required for living-like control over polymerization (e.g., rate of initiation ≫ rate of propagation, absence of termination events), three modes of chain transfer are also prominent for ROMP of CP due to the low strain, decreased reactivity, and relative accessibility of the backbone olefins (Figure 2). Recently, large strides have been taken with regards to mitigating these acyclic metathesis events. Mulhearn et al., using the Mo:PMe$_3$ catalyst system described earlier, determined a kinetic model for controlling the rate of propagations versus inter- and intrachain cross metathesis (Figure 2).[50] This model accounted for the reversible binding rate of PMe$_3$ to the active chain ends and, under optimized synthetic procedures, produced PCP at very high molar mass (M_n > 150 kg mol^{-1}) while maintaining low $Đ$ (≈1.15). Also reported is a very scrupulous method of CP purification to remove acyclic olefin impurities; their ability to undergo chain transfer (Figure 2, left) is a highly competitive side reaction, and their removal is critical for obtaining high M_n.[50] Although successful intra- and interchain metathesis (Figure 2 middle, right) is still a viable reaction for the highly active Mo catalysts, especially at ambient temperature. Their synthetic procedures required high dilution of the growing chain ends (i.e., high monomer to catalyst ratios) and termination at low conversions (~25%) where the concentration of PCP olefins remains low.[50]

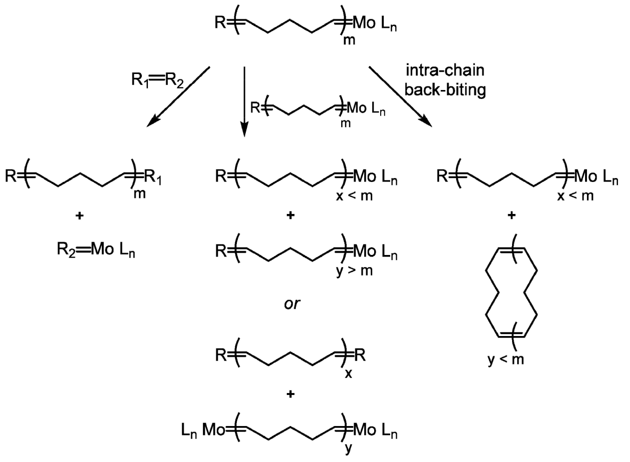


Figure 2. Deleterious acyclic metathesis reactions that lead to loss of living-like control. Left: chain transfer to olefin-containing small molecule (contaminant). Middle: Interchain cross metathesis. Right: Intrachain cross metathesis. Reprinted with permission from ref 50. Copyright 2017 American Chemical Society.

Ru-based catalysts are well-known to be less active, allowing for more functional group tolerance but seemingly at the expense of reduced performance on low-strain monomers and at colder temperatures. Due to the fact that high-strain monomers have been most actively used in Ru-ROMP, many studies involving kinetics and initiation of these catalysts have been performed at ≥25 °C where high conversions are easily obtained. To further understand the behavior of Ru-based catalysts at lower temperatures, we investigated the progression of CP ROMP over time under a variety of conditions. It was discovered that a majority of the polymerizations, when initiated and propagated at $-15\ °C \leq T \leq 0\ °C$, exhibited a very high initial *Đ* which decreased over time.[51] This suggests that initiation rate is slow compared to propagation rate, and this was further suggested by the final M_n being much higher than theoretical based on conversion (Figure 3a, to 3b).[51]

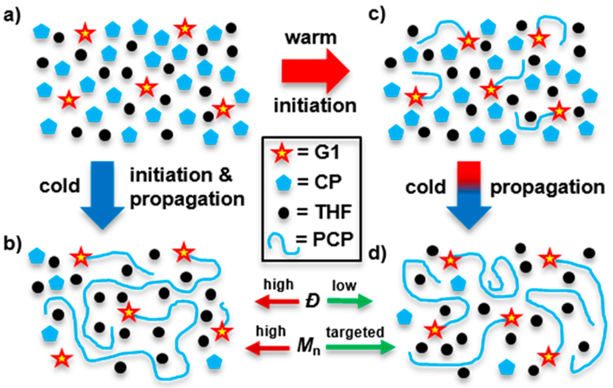


Figure 3. Cartoon concept of variable-temperature (VT) ROMP of CP using G1 in THF. Cold initiation and propagation (a to b) results in poor initiation, higher than theoretical M_n, and high *Đ*. Warm initiation (a to c) results in favorable initiation rate but low conversion. However, subsequent cooling of the reaction after warm equilibrium (c to d) continues propagation to high conversion. Since chain transfer is discovered to be sequestered at 0 °C, the result of VT-ROMP is targeted M_n, narrow *Đ*, and high conversions.

Based on these observations, we hypothesized that a higher starting temperature would suffice to initiate CP effectively, albeit to low conversion (Figure 3a to 3c), and then a subsequent cooling of the reaction would drive thermodynamics to higher conversions (Figure 3c to 3d). This technique, which we termed variable-temperature (VT) ROMP, was optimized through a design of experiments with varying catalysts and solvent used.[52] Narrow *Đ* (∼1.15) and targeted M_n (<5% from theo.) were obtained when using G1 catalyst in THF solvent.[52] Precedence in the literature suggests that THF can weakly coordinate to the G1 catalyst and slow propagation rates.[53−56] This allows lower *Đ* during the warm initiation and also moderates the rate of propagation during cooling. An unexpected yet exciting outcome of this study was that narrow *Đ* is maintained for at least 5 h at 0 °C using G1 and THF; it indicates that intra- and interchain transfer (Figure 2) is largely eliminated under these conditions.[52] Due to its universality, the VT-ROMP method was also shown to be successful for other low-strain cycloalkane species with suitable ΔH_p for ROMP and presents a method for superior control while also obtaining high conversions.[52,57] Other methodologies may also be successful in ROMP of CP. For example, Mugemana et al. showed that confinement of the Ru catalyst on multiarmed polystyrene cores had a dramatic effect on improving G2 tolerance in air and providing a potential route to PCP under facile conditions.[58]

Functionalizing the Five-Carbon Topology. Substituents on the CP ring result in varying possibilities for introducing functionality onto the polymer microstructure. Each presents challenges and opportunities depending on monomer design. The most straightforward method to functionalize PCP is to perform postpolymerization modification to the backbone olefins (Figure 4a). This strategy was the subject of extensive reports (hydrogenation, ionization, hydroformylation, etc.) through the 1970s.[59−62] Recently, Buchmeiser and co-workers performed hydrobromination and hydroboration chemistry on PCP along with further modifications (hydroxylation, amination, and grafting) to access functional polar olefins with a large range of glass transition temperature, T_g, values (−45 to 50 °C) depending on the type and extent of functionality.[63] Although an elegant and facile method for producing a variety of properties, precision topologies are lost due to the propensity for incomplete functionalization and nonregioselective alkene

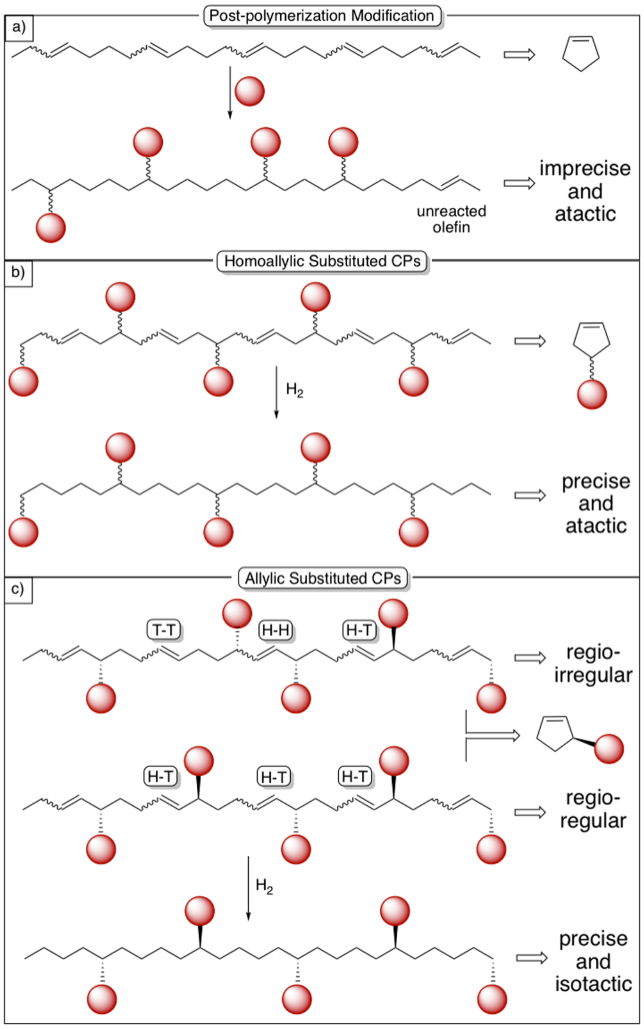


Figure 4. Microstructural outcomes of functionalized polypentenamers from (a) postpolymerization modification of PCP, (b) homoallylic-substituted CP monomer, and (c) enantiopure and allylic-substituted CP monomer.

addition (Figure 4a). Nevertheless, any olefin modification or cross-linking chemistries amenable to 1,4-polybutadiene rubbers should be equally facile for PCP.

Homoallylic Substituents. For precise five-carbon functional spacing, homoallylic-substituted CP monomers are the logical choice. The symmetry of the monomer guarantees precision regardless of the direction of monomer insertion on the metal−alkylidene (Figure 4b). The resulting polypentenamers contain *both* functionality and olefin chemistries. The latter will impart different properties depending on the *cis*/*trans* ratio and can be further cross-linked or chemically modified as discussed earlier. Mild hydrogenation produces polyethylene with exact five-carbon branching, making such materials model compounds for structure−property relationships of precision polyolefins bearing the odd-branch spacing. One limitation of the homoallylic substituent is that the achiral monomer is predicted to yield atactic polymers. The ability to produce a preferred tacticity would require governance on the direction of monomer insertion and may be possible from judiciously designed ROMP catalysts that are chiral or sterically hindered given that CP is prochiral and one face of the ring bears the substituent. However, such a strategy has yet to be reported.

A large majority of experimentally investigated CP monomers have featured the homoallylic substituent (Table 1). As discussed earlier, substitutions on the ring are likely to complicate accurate predictions on ROMP thermodynamics. Al-Hashimi and Bazzi, in collaboration with Tuba and Grubbs, have been taking recent strides toward better prediction on ring strain values of substituted CP monomers using density function theory (DFT) calculations (B3LYP/6-31G).[64−67] Their results predicted 3-cyclopenten-1-ol (**1**) to have a higher ring strain (ΔH_{calc} = 28.33 kJ mol^{-1}) than unsubstituted CP (ΔH_{calc} = 23.76 kJ mol^{-1}). Experimental results confirmed **1** to have a higher ΔH_p (25.94 kJ mol^{-1}) versus CP (ΔH_p = 22.59 kJ mol^{-1}).[67] While these isodesmic equations provide relative strain comparisons between various substituted CP monomers, they may not fully encapsulate all of the thermodynamics associated with ROMP. Experimental determination of thermodynamic values simultaneously provides both ΔH_p and ΔS_p and has also provided additional insight into the sensitivity of these reactions to T.

Table 1. Thermodynamic Results for Select Homoallylic-Substituted CP Monomers

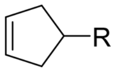
ID	 R =	T_c (1 M)	% conv (2.25 M)			Ref.
			40 °C	0 °C	-20 °C	
1a	-OH	54	71	93	97	67
1b	-OH	49	61	81	88	68
2a	-H	29	38	83	93	34
2b	-H	35	50	83	91	68
3	$-CO_2C(Me)_2Br$	30	41	84	93	57
4	$-OSi(Me)_2(t\text{-}Bu)$	30	42	83	92	68
5	-Ph	-5	0	47	75	51
6	$-CO_2Bn$	-14	0	27	64	68
7	-OBn	-14	0	35	63	68
8	$-CH_2OBn$	-16	0	30	60	68
9	$-CH_2OH$	-25	0	0	46	68
10	$-CO_2Me$	-26	0	4	46	68
11	-COOH	-35	0	0	29	68

Table 1 displays ceiling temperature, T_c, values (M_0 = 1 M) for a variety of homoallylic CP monomers that have been investigated experimentally. The ΔH_p and ΔS_p values were determined by monitoring equilibrium monomer concentration, $[M]_e$, as a function of inverse T by VT-NMR using the linear expression shown in eq 2.[34,51,57,67,68]

$$\ln[M]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R} \tag{2}$$

These thermodynamic parameters allow further calculation of the anticipated % conversion at varying T and M_0, which is beneficial for rational design strategies. Exemplified in Table 1, the substituents on CP have a dramatic effect on their ROMP thermodynamics, and the size of the substituent alone does not appear to have a direct correlation on their polymerizability. For example, when comparing the bulky bromoisobutyryl (BIB) substituent (**3**) with the significantly less bulky hydroxymethyl (**9**),[69] the latter has a T_c that is 55 °C lower! Table 1 also shows the pronounced sensitivity of CP ROMP to both concentration and temperature. The benzyloxymethyl substituent (**8**), while having a T_c of −16 °C at 1 M, is predicted to increase from 0 to 60% conversion between 40 and −20 °C, respectively, at 2.25 M. Here we note that 2.25 M was chosen for these comparisons as this was the concentration most often used during our VT-ROMP studies.[52] Even higher conversions can be expected when increasing monomer concentrations closer to bulk. Finally, a comparison of the thermodynamic parameters determined from two different studies on (**1**) and (**2**) is shown. These comparisons show the sensitivity of these polymerizations to different thermodynamic outcomes, especially for **2a** and **2b** which were performed in the same solvent (THF) and with the same catalyst (G2).[67,68]

Allylic Substituents. CP monomers with allylic substituents are significantly less explored and present unique opportunities for highly precise and isotactic polymers. An overarching challenge lies with the deleterious effects that the substituents can have on the polymerizability of the monomer. Certain groups, such as acetoxy, render the monomer incapable of ROMP even at colder temperatures and higher concentrations.[49,70] On the other hand, methyl,[71] hydroxyl,[70] and trialkylsiloxy[70] substituents have been shown to be viable for ROMP to moderate conversions. Since allylic-substituted monomers are chiral, this presents the opportunity to polymerize enantiopure monomers into isotactic polypentenamers when coupled with regioselective (e.g., head-to-tail) monomer insertion (Figure 4c). An early communication by Sita bolstered this concept through successful ROMP of (*R*)-3-methylcyclopentene using a Schrock Mo-type catalyst yielding ∼60% conversion at −30 °C.[71] The resulting polypentenamers contained ∼70% *trans* olefins and propagated exclusively through a head-to-tail mechanism as determined by NMR.[71] No thermal properties, such as semicrystallinity, were investigated, and no reports followed. The ability for allylic-substituted *cis*-cyclooctenes to influence both the direction of monomer insertion and the resulting *cis*/*trans* ratio of polyoctenamers from Ru catalysts was described by Kobayashi et al.[72−74]

Building on these discoveries, our group recently synthesized cyclopent-2-ene-1-ol and subsequently protected the alcohol with trimethylsilyl (TMS) or triethylsilyl (TES) groups to systematically increase the steric bulk of the substituent.[70] It was discovered that bulky 3-triethylsiloxycyclopentene undergoes ROMP up to 60% conversion at −10 °C in the presence of HG2 in toluene and produces a material that is 92% regioregular (head-to-tail) with 96% *trans* olefins.[70] By synthesizing an enantiomerically enriched monomer (∼92% ee), highly isotactic, *trans*, and regioregular polypentenamers were produced, as confirmed by NMR (Figure 5).[70] Although the material was amorphous (T_g < 70 °C), presumably due to the large size of the TES group, deprotection and mild hydrogenation stand to produce a precision, isotactic, ethylene-vinyl alcohol (EVOH) copolymer derivative. Current synthetic and analytical efforts are underway in our lab to explore this and more isotactic microstructures with a 5-carbon branch spacing.

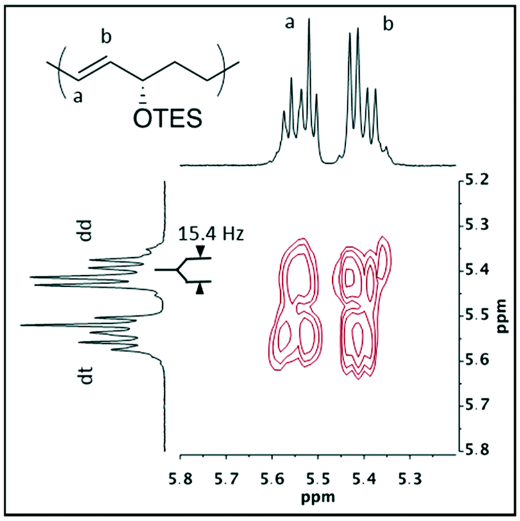
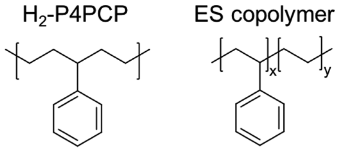


Figure 5. $^1H-^1H$ correlated spectrum of olefin proton signals from a 92% isotactic, 92% regioregular, and 96% *trans*-polypentenamer (M_n = 30 kg mol^{-1}) produced from (*S*)-3-triethylsiloxycyclopentene. The signals show clear doublet-of-doublets (dd) and doublet-of-triplets (dt) splitting due to the highly precise microstructure. The coupling constant of 15.4 Hz is consistent with the *trans* structure. Reproduced from ref 70 with permission of the Royal Society of Chemistry.

Beyond Just Synthesis. With synthetic progress taking large strides, exploration of thermal and physical properties toward potential applications for functionalized polypentenamers is highly needed. Fan and co-workers recently reported a series of homoallylic ester or thioester-substituted CPs where they systematically increased the size of the ester pendant alkyl group.[75−77] The T_g of the resulting polymers was shown to decrease from −26 °C to −65 °C as the ester pendant was increased from methyl to *n*-octyl.[76] With *n*-dodecyl pendants and higher, semicrystalline properties arose from the long alkyl chains.[76] Thioester-containing polypentenamers with similar pendant alkyl groups showed higher T_g and T_m but reduced thermal stability.[77]

Our group's entry point to polypentenamers research came from the ROMP of 4-phenylcyclopentene (**5**) to produce a precision styrenic rubber (P4PCP) or ethylene-styrene (ES) "like" copolymer (H_2−P4PCP) following hydrogenation (Figure 6).[51] Here we reemphasize that, due to the 5-carbon phenyl branch spacing, accessing this microstructure through ES copolymerization is not possible. P4PCP and H_2−P4PCP are rubbery amorphous materials with a nearly identical T_g (17 ± 2 °C) just below ambient temperature which is a key attribute for sound and vibration dampening materials.[78] Further exploration of the viscoelastic and mechanical properties revealed that both share similar density ($\rho_{24^\circ C}$ = 1.03 ± 0.01 g cm^{-3}), but P4PCP has a much higher entanglement molar mass (M_e = 10.0 kg mol^{-1}) versus H_2−P4PCP (3.6 kg mol^{-1}) leading to differing mechanical properties at similar M_n.[79] H_2−P4PCP, which can be likened to an ethylene−styrene (ES) copolymer with exactly 71.4% w/w styrene, is a model material for studying property differences between precise and imprecise microstructure. ES copolymers with similar S content (68−72% w/w) have a higher T_g and lower M_e which subsequently has a large effect on mechanical properties compared to H_2−P4PCP (Figure 6).[80−83] Furthermore, these values vary considerably with only a 4% difference in S content, and mechanical properties vary greatly given the proximity of T_g to ambient. H_2−P4PCP is predicted to have consistent properties from batch to batch due to its high microstructural precision, which is a notable advantage.



	H_2-P4PCP	ES copolymer
%S (w/w)	exactly 71.4	68 - 72
T_g (°C)	17 ± 2	22 - 33
ε (%)	2497 ± 76	292 - 412
E (MPa)	0.85 ± 0.06	10.6 - 741
M_e (kg mol^{-1})	3.62	1.76 - 2.04

Figure 6. Comparison between precise and imprecise phenyl branch spacing on glass transition temperature (T_g) entanglement molar mass (M_e), strain at break (*ε*), and Young's modulus (*E*). Mechanical testing was performed on multiple bars at 23 ± 2 °C. Statistical ES copolymers previously reported display higher values, which vary greatly with only a 4% difference in composition. Values are from ref 79.

Toward Advanced Architectures and Materials. Very recent polypentenamer research has been aimed toward more advanced architectures and function. Poly(styrenesulfonate), PSS (Figure 7a), is a commonly used and ubiquitous polyelectrolyte for applications ranging from ion exchange resins[84] to conducting polymers.[85] When PSS is quantitatively sulfonated, it may be considered a precision polyelectrolyte with an ionic charge placed at every 2 carbons along the chain. Reducing the charge density by reducing the degree of sulfonation would be expected to occur in a random fashion. H_2−P4PCP (Figure 6), when quantitatively sulfonated, would produce a PSS derivative (p5PhS-H, Figure 7a) with reduced charge density at a precise topology. Nearly complete sulfonation (95%) of H_2−P4PCP raises the T_g from 17 to 109 °C, which remains well below the thermal decomposition temperature, T_d (215 °C), where 5% mass loss occurs under

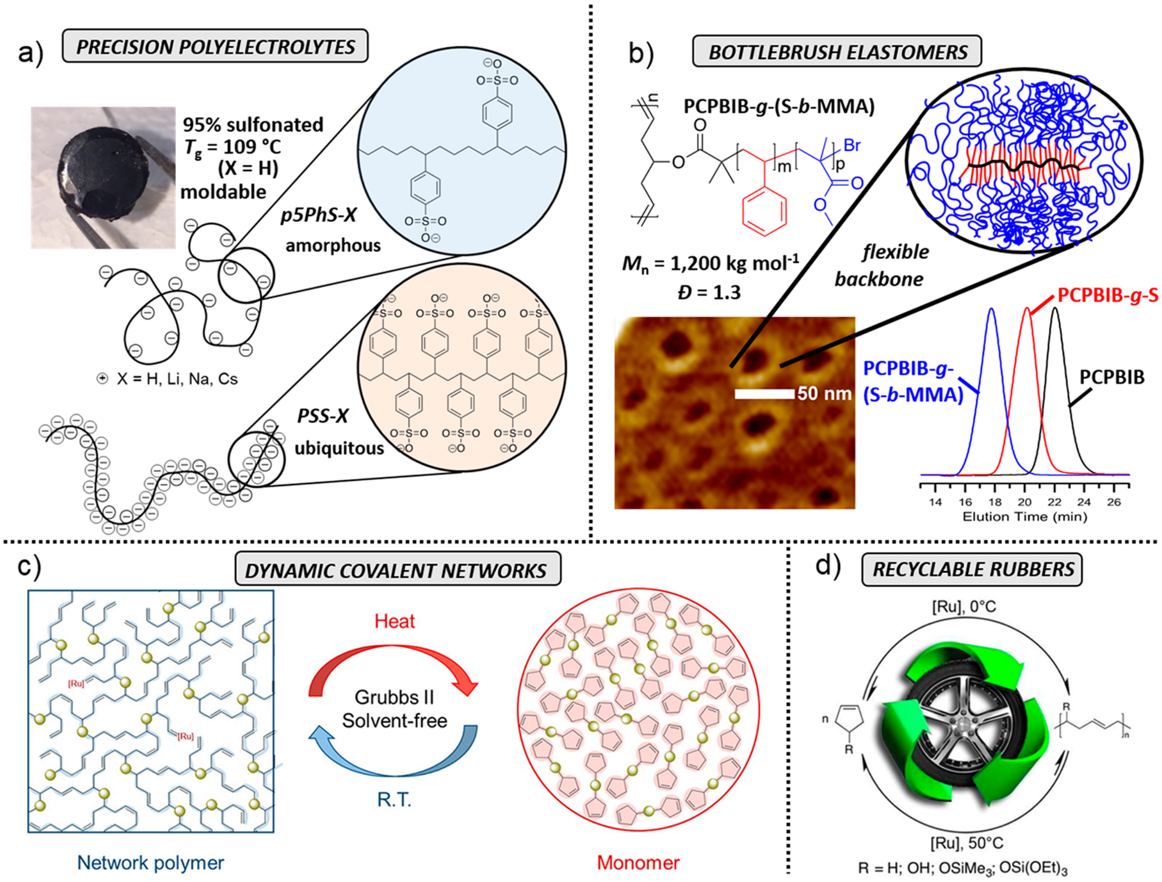


Figure 7. (a) Sulfonation of H_2−P4PCP produces a precision polyelectrolyte similar to polystyrenesulfonate (PSS) but with precise 5-carbon distances along the chain. This material has an accessible T_g (109 °C) allowing it to be thermally molded (inset). Adapted with permission from ref 86. Copyright 2018 John Wiley and Sons. (b) Design of a polypentenamer bottlebrush polymer from ROMP of BIB-functionalized CP followed by ATRP. Block polymer grafts of PS and PMMA, monitored by SEC traces, produce a core−shell polymer visualized by AFM (inset). Adapted with permission from ref 57. Copyright 2018 American Chemical Society. (c) Difunctional CP monomers in the bulk can form dynamic covalent networks that reversibly polymerize and depolymerize upon cooling and heating, respectively. Adapted with permission from ref 68. Copyright 2018 American Chemical Society. (d) Siloxy-functionalized CP monomers produce synthetic rubbers after ROMP which have potential applications in tire technology. These materials recycle back into their original monomer upon heating. Adapted with permission from ref 65. Copyright 2016 American Chemical Society.

nitrogen.[86] By comparison, fully sulfonating polystyrene raises the T_g from 100 °C to a temperature well above T_d.[87] Therefore, p5PhS-H can be thermally molded in the dry state into films or pellets (Figure 7a, inset),[86] while PSS-H requires solvent casting. Aside from melt processing, this material invokes curiosity on how an increased, yet precise, ion spacing will affect many of the applications that PSS is used for; what happens to ion transport, conduction, or transference? How do these precisely spaced ions aggregate in the amorphous state? Such materials open the door to answer these questions.

Bottlebrush polymers (BB) are a rapidly developing area of polymer science.[88−92] To date, there has been severe limitation on the number of backbone options capable of producing densely grafted systems. Mainly, BB systems are produced through polymerizing vinyl-terminated or NB-terminated macromonomers.[88,89] These produce BBs where the number of backbone atoms between each graft (n_g) is 1 or 4, respectively. A CP-terminated macromonomer would also produce $n_g = 4$; however, the polypentenamer BB backbone is much more flexible than the polynorbornene backbone. This is exemplified by the disparity in their T_g values (PCP ≈ −44 °C vs PNB ≈ 45 °C).[63,93] Many theoretical and experimental treatments are focused on how the BB backbone extends to accommodate the increased occupation of pervaded volume by the grafts as they become larger.[94−96] Therefore, the polypentenamer BB backbone, with its high flexibility, is predicted to have a more sensitized response to this phenomenon and may unlock new regimes of material properties for densely grafted systems.[96] Using the VT-ROMP method, our group reported near living-like control over the polymerization of 3-cyclopentenyl α-bromoisobutyrate (**3**) using THF and G1.[57] Subsequent use of the bromoisobutyryl pendants as initiation sites for atom transfer radical polymerization (ATRP) produced the polypentenamer BBs with homopolymer and BCP grafts for the first time (Figure 7b).[57] We confirmed that the backbone polypentenamer macroinitiator (PCPBIB) could be synthesized to targeted molar mass and low Đ with the VT-ROMP method, while ATRP resulted in quantitative "grafting-from" of polystyrene (PCPBIB-*g*-S). It was discovered that the T_g of this material is highly sensitive to graft length, increasing from 4 to 92 °C when traversing side chain degree of polymerization (N_{sc}) from 0 to 18. Subsequent block polymerization of methyl metacrylate (MMA) produced PCPBIB-*g*-(S-*b*-MMA), with high molar mass (M_n = 1200 kg mol^{-1}) and relatively low Đ (∼1.3). These core−shell structures (∼40 nm in diameter) were visualized by atomic force microscopy (Figure 7b). Current aims are to explore the properties of this new BB in comparison to well-established systems.

The same thermodynamic principles that make CP a challenge for ROMP can also be leveraged advantageously to depolymerize PCP systems at higher temperature in the presence of metathesis catalysts. The reversible nature of polypentenamers was first discovered in 1972.[33] Later, Schrock et al. applied high vacuum to a CP polymerization in progress to remove CP monomer and drive equilibrium toward depolymerization.[35] It was discovered that 82−86% of the W catalyst, with its original initiating alkylidene, was recovered.[35] More recently, Tuba et al. designed siloxy-functionalized polypentenamers and explored their potential use as recyclable tire materials.[65] These materials are proposed to increase the polymers' affinity to silica filler (22% makeup of tires with carbon black) and can be fully depolymerized at moderate temperatures (40 °C) in the presence of Ru catalysts (Figure 7d).[65] The reversible nature of polypentenamers has also been used advantageously in reversible bulk networks. Liu et al. investigated a series of CP monomers (Table 1) to determine which low ring strain CP monomers would be optimal for polymerization−depolymerization in the bulk state.[68] By then synthesizing di- and trifunctional CP derivatives, a network polypentenamer could be produced at room temperature that reversibly depolymerizes upon heating (Figure 7c).[68] These covalently adaptable networks (CANs) were shown to reversibly increase in storage modulus from $>10^5$ to <10 Pa between 25 and 55 °C, respectively.[68]

Future Outlook. As we quickly approach the 100 year anniversary of Staudinger's macromolecular theory,[97] there still is much to learn about structure−property relationships. Research on polypentenamers bearing a variety of precise functionalities has matured to a crossroads where more work is warranted to elucidate the value of these materials. Nevertheless there are still experimental designs that are unexplored, like high-pressure CP ROMP and CP ROMP within flow. For the latter, one can imagine that varying the temperature along regions of flow could be quite useful. Explorations of new monomers will surely expand the potential for these systems. For example, recent progress has been made in ring-opening polymerization (ROP) of low-strain 5-membered lactones.[98] Can CP monomers containing heteroatoms in the ring be polymerized? More is being learned about the behavior of common ROMP catalysts at cold temperatures now that cooling these reactions is necessary for high conversions. However, continued catalyst development is also warranted to improve initiation kinetics versus propagation and reduce chain transfer events. Recently, Vanadium catalysts have shown viability for ROMP of CP.[99] Aside from homopolymerization, CP has utility as a comonomer for advanced ROMP strategies such as alternating ring-opening metathesis polymerization (AROMP)[100−102] and cascade or multiple olefin metathesis polymerization (MOMP).[103] Continuing to explore the phenomenologies of CP ROMP may advance these strategies and potentially unlock others.

We now have methodologies to make a variety of polypentenamers with good control, high yield, and readily available catalyst systems. Insight on the physical and material properties is highly needed. What happens to the properties of a vinyl polymer when its functional branches are spaced out to every five carbons? At this point we can rationally hypothesize that these materials will retain the branch functionality, have a lower T_g, remain amorphous (when atactic), have a higher hydrophobicity, and have a reduced M_e. It is our opinion that such materials could serve as improved if not transformative replacements for many plastics that require plasticization.

In addition to their stand-alone material properties, the rich thermodynamics of polypentenamers is presenting opportunities to leverage their low T_c for recyclable materials, self-immolative systems, and thermally reversibile networks. Near living-like polymerizations have ushered in advanced architectures from CP systems, such as BB and BBCP, and more hierarchical structures are certainly warranted to increase the diversity of polypentenamers within frontier materials.

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ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 1750852. The authors wish to thank Prof. Marc Hillmyer and Dr. Gabriel dos Passos Gomes for helpful discussions. We also thank Prof. Jeffrey Moore and Huiying Liu for providing additional details on the thermodynamic values of substituted CP derivatives. W.J.N. wishes to thank Sue Neary for artwork contributions.

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