Conference paper

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Synthesis of cyclopolyolefins via ruthenium catalyzed ring-expansion metathesis polymerization

Abstract: Polymers exhibiting cyclic topology have attracted great interest over the past 30 years. Macrocycles or cyclopolymers with more than 20 repeating monomer units are considered exceptional candidates for thermoplastic engineering application due to unique properties in comparison to their linear analogues including large hydrodynamic radii and functional group density, heat resistance, good insulating ability and low intrinsic viscosity. Cyclic polymers are thus expected to exhibit improved physical and mechanical properties for certain applications due to the absence of end groups. Although synthetic challenges have historically limited research on cyclic polymers, recent developments in ruthenium catalyzed ring-expansion metathesis polymerization (REMP) have enabled the synthesis and the preliminary investigation of structure-property relationships of high molecular weight macrocycles. In REMP reactions the polymer formation is proposed to proceed through a transient macrocyclic complex in which both ends of the growing polymer chain remain attached to the Ru center. This article summarizes the recent discoveries on the field of REMP assisted cyclopolymer based material development.

Keywords: cyclopolyolefins; POC-2014; ring-expansion metathesis polymerization; ruthenium.

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Introduction

Subtle topological differences between cyclic and linear polymers manifest as significant changes to material properties. Restricted conformational degrees of freedom and associated increases characteristic chain dimensions on the molecular length scale lead to macroscopically distinct physical properties [1], such as lower viscosity and higher thermal stability [2]. Architectures with well-defined dimensions may thus provide significant advancements in fields such as nanotechnology and material science. However controlling high molecular weight polymer topology still presents challenging tasks for synthetic chemists [3–8].

Synthetic procedures in general include ring closure and ring-expansion techniques. In ring closure the cyclic polymers can be synthetized either by ring-chain equilibration or highly efficient coupling of end-functionalized linear polymers. The ring-chain equilibrium reactions include transesterification (polyesters) [9], transamidation (polyamides) [10], transimidation (polyimides), and transetherification (polyarylethers) [11]. In general when backbiting occurs, two lower molecular weight polymers form from a single a linear polymer chain: a cyclic and a shorter linear one. When coupling reactions are applied in an intramolecular reaction

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Scheme 1 Ring-expansion metathesis (REMP) catalysts tested for cycloolefin synthesis.



Scheme 2 Mechanism of ROMP reactions.

 α, ω end-functionalized polymers are used to form a cyclic polymer. The molecular weight of the formed cyclic polymers remains similar to its starting end-functionalized linear analogue. The coupling reactions are often carried out with use of catalysts or coupling agents. The main drawback of these synthetic procedures is the necessity of highly diluted condition and difficult separation of cyclic polymers from unreacted linear contaminants.

Several ring-expansion polymerization (REP) techniques have also been explored including cyclic polyesters from cyclic N-heterocyclic carbene initiators [12], insertion of methylene into the cycloboroalkanes [13] and chain transfer polymerization of cyclic dithioesters [14]. The main advantages of the REP polymerization processes – where the overall circularity of the systems is maintained over the polymerization – are the elimination of both linear intermediates and the high dilution [15–19]. For instance, ring-expansion metathesis polymerization (REMP) is capable of producing high molecular weight macrocycles from readily available cyclic monomers using metallacycle ruthenium catalysts [20, 21].

The REMP reaction is a special type of the ring-opening metathesis polymerization (ROMP) reaction initiated by metallacyclic ruthenium carbene pre-catalysts (Scheme 1).

Ruthenium based alkene metathesis catalysts have been extensively studied mechanistically [22]. Equilibrium ROMP reactions (Scheme 2) are driven by release of cyclic monomer ring strain during polymerization. For example, it is not possible to ROMP cyclohexene as its ring strain energy is close to 0 kcal mol⁻¹, however, the highly strained *trans*-cyclooctene (16.7 kcal mol⁻¹) is readily polymerized quantitatively [23]. Cyclopentene ring offers insight into intermediate ring strain behavior; the ring is moderately strained (6.8 kcal mol⁻¹) [24] and thus forms an equilibrium mixture at room temperature (in Scheme 2, k_3 and k_4 are nearly equal) [25]. Due to the negative and moderately large ΔS , the equilibrium concentration of cyclopentene is quite temperature dependent. ROMP (and REMP) reactions are thus most efficient for highly strained cycloolefines.

This paper focuses on ruthenium catalyst promoted REMP reactions and aims to assist in the development of large molecular weight cyclopolymer synthetic strategies for future polymer and advanced material developments. The REMP reactions discussed include the synthesis of novel materials such as cyclopolyolefines, cyclobrush polymers and dendrimerized cyclopolyolefins. Limitations and related challenges are also discussed.

Cyclic polymers synthetized by ruthenium catalyzed REMP

The first cyclic ruthenium REMP catalyst (Scheme 1) was synthetized by Fürstner [26]. Addition of metallacyclic REMP catalyst **1** to *cis*-cyclooctene (COE) in solution at 40 °C resulted in the formation of polyoctenamer (Scheme 3). Following the insertion of a predetermined amount of monomer into the metallacycle ring, the macrocyclic complex underwent intramolecular cross-metathesis to yield cyclopolyoctenamer and the start-



Scheme 3 Synthesis of cyclic polyoctenamer using ring-expansion metathesis (REMP) catalyst.

ing catalyst. The polymerization was complete after 12 h. A variety of polymers up to 1200 kDa have been synthesized by varying the monomer/catalyst ratio. As expected the molecular mass dispersities (Đ) were around 2.0. The isolated polymers were hydrogenated using palladium catalyst to afford cyclic polyethylene [20]. Following the preliminary investigations a series of cyclic Ruthenium-alkylidene complexes were synthesized and tested for ring-expansion metathesis catalysis (REMP) (Scheme 1). The modular catalyst design provided ruthenium complexes having electronically different NHC ligands, as well as varying tether lengths. The catalyst activities were tested via COE polymerization. The impact of the tether length on the polymerization rate has been investigated; shorter tethers had profound effects on the intramolecular chain transfer and cyclopolymer release [27]. Furthermore saturated NHC backbone ligands increase polymerization rates. In conclusion, ruthenium complexes bearing saturated NHC ligand and five or six carbon tethers proved to be the most suitable catalysts for the synthesis of high molecular weight cyclopolyoctenamers [28].

Polymerization conducted with five-carbon tethered catalyst (Scheme 1) led to a step-growth mechanism with a sharp steep increase after 95 % conversion. Six-carbon tethered catalyst however showed a different weight-average molecular weight versus monomer conversion plot. Rapid molecular weight growth resembled a chain-growth polymerization mechanism reaching a maximum 70 % monomer conversion. The mechanistic differences were explained by a significant competition between propagation and five-carbontethered catalyst release from growing polymer ring [27]. Equilibrium ROMP of COE with five- and six-carbontethered catalyst resulted in high molecular weight (60–120 kDa) cyclopolymers, which were independent from the applied catalyst structure.

The ROMP of cyclooctadiene (COD) using REMP catalyst **1** was also investigated at elevated temperature (45 °C) (Scheme 4). Polymers with different range of molecular weight were synthesized by varying the initial monomer/catalyst ratio. Varying the monomer initial concentration could also modify the polymer molecular weight. At highly dilution (M < 0.1 M), only low-molecular weight oligomers were observed [21].



Scheme 4 Synthesis of cyclopolybutadiene using cyclooctadiene (COD) and ring-expansion metathesis (REMP) catalyst 1.

Alternatively cyclopolybutadiene was synthesized using *trans-cis-trans*-cyclododecatriene (CDT) with similar reaction conditions. Varying the monomer/catalyst ratio or initial monomer concentration gave 12–88 kDa molecular weight cyclopolymers. The rate of monomer consumption was fast, $\tau_{1/2} = 10$ min with concomitant rapid increase in polymer molecular weight. The polymer microstructure prepared using either COD or CDT had predominantly *trans* olefin geometry and 1,4-regioisomer [21]. Depolymerization of the polymers was observed by a slow decrease of molecular weight over time, which equilibrated after 12 h. The dispersities of the polymers were around 2.0, which is also typical for equilibrium-controlled polymerizations.

Synthesis of cyclic polymer based advanced materials using ruthenium catalyzed REMP

The REMP of 5-acetoxy-1-cyclooctene (ACOE) using six-carbon-tethered catalyst **2** led to high molecular weight poly-5-acetoxy-1-cyclooctene (PACOE) (Scheme 5). Thiol-ene chemistry [29, 30] assisted cross-link of the cyclopolymer internal double bonds created an innovative material with a unique structural unit. The properties of the cross-linked cyclic PACOE gels were notably different from those of cross-linked linear analogue. For example the swelling ratio of the cyclopolymer related gels simultaneously increased with decreasing initial polymer concentration in the gel solution, which is unlike to its linear analogue, where a decreased swelling ratio was reported. Furthermore the maximum strain at break of the cyclopolymers based gels was always greater than linear-polymer derived gels. The more compact cyclopolymers were speculated to contain more inter- than intramolecular cross-links compared to the analogous linear polymer gels [31].

Brush polymers represent an important class of macromolecular architectures [32, 33]. However cyclic brush polymers that exhibit toroidal nanostructures remain rare. The synthesis of ultrahigh molecular weight cyclic brush polymers using a REMP catalyst with saturated NHC ligands and macromonomers (MM, ω-norbornenyl polysterene) have been reported [34]. Extremely high, 1900–26 000 kDa molecular weight polymers were obtained, which were visualized by atomic force microscopy (AFM) (Scheme 6) [35].

AFM investigation [36] has shown the cyclic brush structures exhibit diameters in the range of 100–180 nm, which corresponds to 310–560 nm contour lengths. These cyclo brush polymers are apparently not stable as the backbone is easily cleaved by mechanical stress [35], in agreement with literature data reported for densely grafted linear polymers [37, 38].

A synthetic approach for the synthesis of versatile functionalized cyclopolymers is the incorporation of clickable chemical groups into cyclic polymers. This combination of click-chemistry [39] with ring-expansion polymerization techniques provides access to wide range of functionalized cyclopolymers. Alkyne clickable side group containing cyclic polymers have been reported by Tew. The combination of copper (I) catalyzed azide-alkyne click chemistry with REMP demonstrated the versatile synthesis of cyclic polymer brushes and novel network materials containing cyclic molecular architectures. This method provided large cyclic polymer backbone with high purity. Click chemistry is also a very efficient tool for installation of graft polymer side chains and producing novel macromolecular architectures (Scheme 7) [40].



Scheme 5 Synthesis of cyclopolymer based gels using 5-acetoxy-1-cyclooctene (ACOE) via ring-expansion metathesis (REMP) catalysis.



Scheme 6 Synthesis of cyclic brush polymer using ω-norbornenyl polysterene and REMP catalyst saturated on NHC ligands.



Scheme 7 Synthesis of cyclobrush polynorbornene and cross-linked cyclopolynorbornene by "click chemistry."

High molecular weight cyclic brush polymer derivatives can also be synthetized via functionalization of cyclopolymers containing hydroxyl side groups (Scheme 8). Polyester side chains can be grown via ringopening polymerization of cycloesters on the OH functionalized cyclopolymer using triazabicyclodecene catalyst [41].

The polymerization of sterically hindered macromonomers (MM) is rare, however it was shown that the dendronized macromonomer **3** could be effectively polymerized via REMP using more active REMP catalyst saturated on NHC ligands (Scheme 9). Compared to the previously reported polymerization conditions it required higher reaction temperature (55 °C) and catalyst loadings. The isolated polymers had extremely high molecular weight (1970–5330 kDa) with moderate dispersities (1.17–1.51). Interestingly, an inverse relationship between degree of polymerization and reaction concentration was observed presumably due to the higher initiation rate relative to propagation rate with increased reaction concentration [42].

The molecular weight of the dendronized polymer did not change upon addition of fresh catalyst or prolonged standing after 100 % monomer conversion indicating that the polymerization growth is kinetically controlled and not equilibrium. The cyclic topology of the dendronized polymer was confirmed by AFM imaging [36]. Linear polymer impurities were not detected [42].



Scheme 8 Synthesis of cyclo brush polynorbornene via cycloester ring-opening polymerization technique.



Scheme 9 Synthesis of dendronized cyclic polymers using dendronized macromonomers and REMP catalyst saturated on NHC ligands.

Challenges in REMP reactions: Analysis and Linear Impurities

One of the most significant challenges in cyclic polymer chemistry is the definitive proof of the ring topology. The combination of solution-state properties, such as different GPC retention times, hydrodynamic radii, viscosities, and mass spectroscopy analysis is used to discern the cyclic and linear polymer analogues [43–47]. The more compact cyclic polymers have lower intrinsic viscosities and possess smaller hydrodynamic volumes than their linear analogues. In general the ratio of the viscosity for cyclic and liner polymers is circa 0.4 in good solvents [20]. The radius of gyration R_g also depends on polymer topology [2, 20]. Our preliminary investigations indicate that cyclic polypentenamers reveal significantly higher Mark-Houwink "a" parameters compared to their similar molecular weight linear analogues [25], perhaps suggesting increased chain rigidity associate with the cyclic topology (a_{cyclic} : 0.92 ± 0.05; a_{linear} : 0.59 ± 0.04) [48].

Solid or melt state NMR spectroscopy is one of the most powerful methods that can provide qualitative and quantitative information about cyclic polymer topology. Although the sensitivity of solution state NMR spectroscopy is limited because of the low concentration of ¹³C nuclei the melt-state magic-angle spinning (MAS) NMR spectroscopy is suitable method for detecting linear polymer contaminants [49, 50]. Recently, optimized melt-state MAS NMR methodology has been developed for quantitative analysis of branched poly-ethylene polymers [51, 52].

The cyclic topology of ultrahigh molecular weight dendronized and brush polymers can also be confirmed by atomic force microscopy (AFM). However the visualization of non-functionalized polymers is still remaining a challenging task. Although this method is one of the best qualitative tools it cannot provide quantitative information about the ratio of the cyclic-linear species. Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry is also an important analytical tool for cyclopolymer analysis [20]. MALDI-TOF was introduced in 1985 and proved to be a break-through technique in high molecular weight polymer analysis [53, 54]. The technique is suitable tool for the investigation of branched- and cyclic polymer analysis and the detection of linear contaminants in the reaction product [55]. The MALDI-TOF assisted polymer analysis is widely used in material science, but analysis of high molecular weight cyclic non-polar polymers remains challenging.

The analysis of low molecular weight cyclopolymers and oligomers can be performed by multiple wavelength HPLC [54, 56], which provides information about the purity of cyclic polymers and possible presence of linear impurity contaminatinants [57, 58].

Although several analytical tools are available for the analysis of cyclopolymers they are mainly limited to analysis of low molecular weight polymers and oligomers, since the uncertainty is often high for large cyclic species. Efficient and reliable analytical techniques, especially for high-molecular weight non-polar cyclic polymers analysis are remained to be undiscovered.

Elimination and/or the efficient separation of linear polymer impurities also are important and unsolved issues for polymer scientists. Although the presented REMP catalysts are powerful tools for the synthesis of high molecular weight polymers they suffer from several drawbacks such as low stability and moderate activity. They often require slightly elevated reaction temperature (40–60 °C) and prolonged reaction time (24 h). These conditions may result in some REMP catalyst decomposition leading to the formation of linear contaminants. The linear impurities not only contaminate the reaction product but also can induce the ring opening of cyclic polymer via ROM chain reaction (Schemes 10 and 11). The longer reaction time presumably leads to higher content of linear polymers.

Thereto date is no efficient technique for the quantitative determination and separation of linear contaminants from their cyclic counterparts reported. However intensive research is ongoing to develop new metathesis catalysts that are highly stable and efficient even at moderate reaction condition. Immobilization of ruthenium metathesis catalysts [59–63] to phase labeled supports can facilitate separation of contaminants produced from catalyst decomposition.

Conclusion

Cyclopolymers are of great industrial interest, since they possess unique physical and mechanical properties. These materials could have wide industrial and commercial application in areas including packaging, medicinal aid, petrochemical and tire production.

One of the most efficient synthetic methodologies to access high molecular weight macrocyclic polymers, ring-expansion metathesis polymerization (REMP), was reviewed here. REMP catalysts are clearly capable of producing cyclic polymers with extraordinarily high molecular weights including cyclic polyoctenamers and polybutadienes, ultrahigh molecular weights (up to 9000 kDa) cyclic brush polymers and dendronized cyclopolymers.



Scheme 10 Ruthenium catalyzed ring-opening metathesis (ROM) of cyclopolyolefines in the presence of linear contaminants.



Scheme 11 General scheme for the linear contaminant induced ring-opening of high molecular weight cyclopolymers.

Although the REMP methodology particularly effective at producing high molecular weight macrocycles, some drawbacks, including relatively low catalyst stability and activity limits its utility. The relatively high catalyst loading needed makes these synthetic procedures expensive and intellectually but not practically interesting. Moreover, linear impurities formed during catalyst decomposition can initiate side cross-metathesis reactions, which result in the formation of undesired linear contaminants. As of today, there is now efficient separation techniques applicable to linear and cyclic polymers thus the development of highly efficient, selective and stable catalyst systems is a powerful approach to eliminate the formation of undesired linear containinants to obtain highly pure and large cyclopolymer based materials. The development of stable and highly efficient catalyst systems and topological analytical techniques are necessary to improve the purity and applicability of large cyclopolymers.

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